

**Development and Application of New Modified  
Poly(styrene-divinylbenzene) Adsorbents and Chromatography  
Stationary Phases**

**Volume 1  
PS-DVB Heptadecyl Ketone, Chloromethyl PS-DVB, and  
Octadecoxy Methyl PS-DVB**

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**End of Project Report  
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## UNIVERSITI TEKNOLOGI MALAYSIA

BORANG PENGESAHAN  
LAPORAN AKHIR PENYELIDIKAN

TAJUK PROJEK: **DEVELOPMENT AND APPLICATION OF NEW MODIFIED  
POLY(STYRENE-DIVINYLBENZENE) ADSORBENTS AND  
CHROMATOGRAPHY STATIONARY PHASES. VOLUME 1:  
PS-DVB HEPTADECYL KETONE, CHLOROMETHYL PS-  
DVB, AND OCTADECYL METHYL PS-DVB**

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## ABSTRACT

Poly(styrene-divinyl benzene) (PS-DVB) resin is an attractive adsorbent for extraction and separation of various types of compounds due to its stability over the pH range of 1-14. However, PS-DVB resin is known to have hydrophobic surfaces that highly retain non-polar compounds while poorly retain polar compounds. To improve its use in the separation or extraction of polar compounds, PS-DVB resin must be chemically or physically bonded to hydrophilic groups to reduce its hydrophobic surface. The objectives of this project were to modify PS-DVB phases by introducing moieties that can increase the dispersive forces and lower the hydrophobicity of the PS-DVB phases and to examine the characteristics and applications of the modified PS-DVB adsorbents.

The PS-DVB adsorbents were prepared by suspension polymerization method with polyvinyl alcohol as the suspension stabilizer at a stirring speed of 1000 rpm for 20 h. In the first approach (Volume 1), the synthesized PS-DVB adsorbents were subjected to modifications that consisted of (i) Friedel-Crafts acylation reaction using stearoyl chloride as an acylation agent to produce PS-DVB heptadecyl ketone, (ii) Chloromethylation reaction to produce chloromethyl PS-DVB in the presence of chloromethyl styrene, and (iii) Williamson ether reaction using sodium metal and octadecanol as reaction agents to produce octadecoxy methyl PS-DVB. The synthesized adsorbents were characterized by FTIR spectroscopy, SEM, nitrogen adsorption analysis and thermogravimetric analysis. Solid phase extraction (SPE) studies of test compounds, namely nitrobenzene, 2-chlorophenol, benzaldehyde, butyrophenone, and *p*-cresol were carried out using SPE tubes packed with the synthesized adsorbents. The recoveries obtained for the home-made PS-DVB were in the range of 7% to 72% with relative standard deviations of 1% to 10%. Increased percentages of recovery (35%-83%) with the relative standard deviations of 2%-7% were obtained using PS-DVB heptadecyl ketone. Highest recovery percentages (67%-100%) were obtained using commercial C<sub>18</sub>-silica adsorbent. Highest breakthrough volume was achieved for PS-DVB heptadecyl ketone adsorbent, i.e. 30.60 mL of 20 ppm nitrobenzene and 20.47 mL of 20 ppm 2-chlorophenol. Lowest breakthrough volume was obtained for octadecoxy methyl PS-DVB adsorbent (1.03 mL of 20 ppm nitrobenzene and 1.00 mL of 20 ppm 2-chlorophenol). PS-DVB heptadecyl ketone has been proven suitable to be used as SPE adsorbent in the future.

## ABSTRAK

Resin poli(stirena-divinil benzena) (PS-DVB) merupakan penjerap yang menarik untuk pengekstrakan dan pemisahan pelbagai jenis sebatian disebabkan kestabilannya pada julat pH 1-14. Walau bagaimanapun, resin PS-DVB diketahui mempunyai permukaan yang hidrofobik yang sangat menahan sebatian tak berkutub manakala tidak menahan sebatian berkutub. Untuk memperbaiki penggunaan bahannya dalam pemisahan atau pengekstrakan sebatian berkutub, resin PS-DVB mesti diikat secara kimia atau fizik kepada kumpulan hidrofilik untuk mengurangkan kehidrofobikan permukaannya. Objektif projek ini ialah untuk mengubahsuai fasa PS-DVB dengan memasukkan moiety yang boleh meningkatkan daya serakan dan mengurangkan kehidrofobikan fasa tersebut dan untuk mengkaji ciri-ciri dan penggunaan PS-DVB terubahsuai itu.

Penjerap PS-DVB telah disediakan dengan kaedah pembolimeran ampai dengan alkohol polyvinil sebagai penstabil ampai pada kelajuan putaran 1000 rpm selama 20 j. Dalam pendekatan yang pertama (Jilid 1), penjerap PS-DVB yang telah disintesis telah dimodifikasi melalui kaedah (i) Tindak balas pengasilan Friedel-Crafts menggunakan stearoil klorida sebagai agen pengasilan untuk menghasilkan PS-DVB heptadekil keton, (ii) Tindak balas pengklorometilan untuk menghasilkan klorometil PS-DVB dengan kehadiran klorometil stirena, dan (iii) Tindak balas eter Williamson menggunakan logam natrium dan oktadekanol sebagai agen tindak balas eter untuk menghasilkan oktadekoksi metil PS-DVB. Penjerap yang telah disintesis itu dilakukan pencirian menggunakan spektroskopi FTIR, SEM, analisis penjerap nitrogen and analisis termogravimetri. Kajian pengekstrakan fasa pepejal (SPE) bagi beberapa sebatian organik terpilih seperti nitrobenzena, 2-klorofenol, benzaldehid, butirofenon dan *p*-kresol dijalankan dengan menggunakan tiub SPE yang dipadatkan dengan penjerap yang disintesis. Pertambahan peratus perolehan semula (35%-83%) dengan sisihan piawai relatif 2%-7% dihasilkan dengan menggunakan PS-DVB heptadekil keton. Peratus perolehan semula yang tertinggi (67%-100%) dihasilkan oleh bahan penjerap C<sub>18</sub>-silika komersial. Penentuan kemunculan isipadu untuk beberapa bahan penjerap menunjukkan bahawa kemunculan isipadu yang tertinggi dihasilkan oleh PS-DVB heptadekil keton, iaitu 30.60 mL untuk nitrobenzena 20 ppm dan 20.47 mL untuk 2-klorofenol 20 ppm. Kemunculan isipadu yang terendah dihasilkan oleh bahan penjerap oktadekoksi metil PS-DVB (1.03 mL untuk nitrobenzena 20 ppm dan 1.00 mL untuk 2-klorofenol 20 ppm. PS-DVB heptadekil keton terbukti sesuai digunakan sebagai bahan penjerap SPE di masa hadapan.

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## LIST OF SYMBOL/ABBREVIATION/NOTATIONS/TERMS

PS-DVB	-	Poly(styrene-divinylbenzene)
SPE	-	Solid Phase Extraction
ppm	-	Parts per Million
GC	-	Gas Chromatography
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transform Infrared
IR	-	Infrared
<i>p</i>	-	Para
μL	-	Micro liter
mL	-	Mili Liter
v/v	-	Volume per Volume
KBr	-	Potassium Bromide
mg	-	Mili Gram
mm	-	Mili Meter
kPa	-	Kilo Pascal
$M_X$	-	Test Compound Concentration (ppm)
$M_S$	-	Internal Standard Concentration (ppm)
$F_S$	-	Internal Standard Response Factor
$F_X$	-	Test Compound Response Factor
$A_S$	-	Internal Standard Peak Area
$A_X$	-	Test Compound Peak Area
$\sigma$	-	Population Variance
$n_1$	-	Size of Sample
$H_0$	-	Null Hypothesis
$H_1$	-	Alternative Hypothesis
$\alpha$	-	Level of Significance
$\nu$	-	Degree of Freedom
$\bar{X}$	-	Mean
$s$	-	Standard Deviation
$t_R$	-	Retention Time
IS	-	Internal Standard

R.S.D.	-	Relative Standard Deviation
ODS	-	Octadecylsilica
%R	-	Percentage of Recovery
$c$	-	Effluent Concentration
$c_0$	-	Influent Concentration
$c/c_0$	-	The ratio of Effluent Concentration to Influent Concentration.
SEM	-	Scanning Electron Microscopy
BET Method	-	Brunauer, Emmet and Teller Method
BJH Method	-	Barrer, Joiyner and Halenda Mehtod
TG	-	Thermogravimetric

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# **CHAPTER 1**

## **INTRODUCTION**

### **1.1 General Background**

Thousands of polymers have been synthesized and more are likely to be produced in the future. Functionalized polymers have found various applications as supports in solid phase synthesis, such as chromatographic packing, polymer supported catalysts and starting materials for the synthesis of ion exchange resins. The suspension copolymerization of styrene with divinylbenzene has been developed by Kun and Kunin [1] to produce poly(styrene-divinyl benzene) (PS-DVB). This material has been widely used as a stationary phase for high performance liquid chromatography (HPLC) and matrices of a great number of ion exchangers.

Previous workers [2] have found that macro-porous PS-DVB is prepared as a result of phase separation during the copolymerization in the presence of inert diluents. The inert diluents are extracted after copolymerization and porous structure is obtained. Polymers, solvents or non-solvents of polystyrene or mixture of them may be used as diluents giving various types of pore size distribution.

PS-DVB copolymers have a hydrophobic surface and overcome many of the limitations of bonded silicas, especially those related to the limited pH stability in the presence of the silanol group [3]. PS-DVB is often used as sorbents in reversed-phase (RP) liquid chromatography [4]. Usually, porous PS-DVB packing materials are employed because they provide a large surface area. Commercially available porous PS-DVB packing includes Amberlite XAD-2, PLRP-S, and PRP-1. While PS-DVB packing has many advantages, such as chemical stability at high and low pH and the absence of residual silanol groups, they suffer from the disadvantage of yielding lower chromatographic efficiencies than silica-based octadecylsilyl bonded phase packing of the same particle size.

Since 1990s, chemically modified resins have been developed and applied to the trace enrichment of polar substances. These sorbents have excellent hydrophobicity and yield higher recoveries than unmodified ones and have found great applications in solid phase extraction (SPE) for sample preparation in environmental analysis [5]. One of the possible chemical modifications of resin is by using Williamson ether reaction. The Williamson ether reaction was named after Alexander William Williamson (1824-1904). The Williamson ether synthesis is an example of a nucleophilic substitution reaction. The nucleophile is an alkoxide anion, which displaces a halide ion, typically chloride or bromide, from a primary haloalkane. The alkoxide can be generated by addition of metallic sodium to the corresponding alcohol. Although the Williamson ether synthesis is a general method for the laboratory production of ethers, there are some limitations to its use. Since the alkoxide ion is a strong base, their use is limited to primary unhindered alkylating agents. Otherwise, elimination competes strongly with the nucleophilic substitution for the reactant molecules. Sometimes, the reaction is run in a solvent, which fosters the  $S_N2$  process [6-7].

Solid-phase extraction has recently come into the focus of interest and offers a viable alternative to the conventional sample preparation methods [5, 8, 9]. SPE has evolved to be a powerful tool for isolation and concentration of trace analytes in a variety of sample matrices. Nowadays, the most frequently used design in off-line SPE is the cartridge or the syringe barrel. They are usually made of polypropylene or polyethylene and filled with packing material having different functional groups.

The solid sorbent is contained between two 20- $\mu\text{m}$  polypropylene frits. Cartridges vary from as little as 100 mg to 1 g or more. Syringe barrels range in size from 1 to 25 mL and packing weights from 50 mg to 10 g. Solvent reservoirs may be used at the top of the syringe barrels to increase the total volume (50-1000 mL) [8].

The breakthrough volumes can describe the characteristics of adsorbents. To record a breakthrough curve, after proper equilibration of the SPE cartridge, a solution of analyte is pumped directly to the detector (cartridge in the bypass position) to determine its absorbance signal. The cartridge is switched in-line causing the UV signal to drop to baseline level because the analyte is retained on the cartridge. Upon breakthrough, the UV signal will rise back to its initial level. The volume of analyte solution that can flow through the cartridge before breakthrough occurs is the “breakthrough volume” and is used as the measure of the extraction capacity [10].

This research was set to explore the methods of preparing of PS-DVB stationary phases, their modification, characterization, as well as application in analytical separation. PS-DVB beads were synthesized based on suspension polymerization from its monomers, styrene, and divinyl-benzene. A new PS-DVB modification method was carried out by introducing octadecoxy group ( $\text{C}_{18}\text{H}_{37}\text{-O-}$ ) onto the PS-DVB backbone.

## 1.2 Problem Background

The beginning of the era of synthetic polymers for ion exchange is generally attributed to the work of B. A. Adams and E. L. Holmes at the Chemical Research Laboratory, Teddington, England [11]. Although the phenomenon of water softening by ion-exchange was known at the time of their collaboration, the deionization of water required stable materials capable of performing both cation and anion exchange.

A polymer is a chemical species of high molecular weight. It is made up of repeating low-molecular weight units. These repeating units are termed monomers and the compounds are reacted to form a polymer. There are two types of polymers namely, natural and synthetic polymers [12]. The PS-DVB polymers are manufactured as general sorbents and they are often chosen for SPE works because the loading properties of organic carbon are superior to those of silica-based adsorbent [13]. Leon-Gonzalez and co-workers [3] have found that the chemically modified PS-DVB resin can adsorb wide variety of organic analytes efficiently. They have a higher sorption capacity for the more polar compounds than their unmodified analogues do.

Balakhrisnan and Ford [14] have found that the suspension polymerization is widely used in polymerization of styrene. The major factors controlling the particle size are surface tension, densities of aqueous and monomer phases, viscosities of aqueous and monomer phases, diameters of stirrer and kettle, and stirring speed. Their research on particle size effects in polymer supported organic synthesis and polymer supported phase transfer catalysis requires cross linked polystyrenes of a wide range of sizes with chloromethyl group that can be converted easily to polymer bound.

Masque *et al.* [5] described the application of unmodified and modified PS-DVB to the analysis of group of polar phenolic compounds. They have used on-line and the off-line SPE to determine pollutants in environmental waters. The advantages of on-line SPE are the higher sensitivity, absence of organic solvents and less manipulation of the samples, which leads to greater precision, and makes it easier for it to be automated. The functional polymer networks have gained great importance in many fields of scientific research as well as for industrial applications. The interest stems from the variety of possible modifications of their chemical and physical properties. Claudio *et al.* [15] said that increasing environmental concerns in waste water treatment has led to the use of organic ligands anchored to solid supports in order to remove and recover important metal ions from aqueous solution.

The use of polymeric resins in reversed-phase high performance liquid chromatography (RP-HPLC) has grown dramatically, since an increasing number of polymeric columns are commercially available. The application of silica-based supports is limited by the low stability of silica at alkaline pH values and by the unwanted interactions between polar solutes and remaining free silanol groups not covered by the hydrophobic ligands. In particular, PS-DVB-based resins show a high stability over the pH range 1-14 and provide excellent separations. Additionally, PS-DVB particles permit the introduction of numerous functional groups that change their surface chemistry and hence the chromatographic selectivity [16].

Porous PS-DVB based resins have proven to be very effective for SPE of a wide variety of organic compounds from predominantly aqueous samples. Their effectiveness is enhanced by chemical introduction of polar groups, such as acetyl, and sulfonic acid [17]. However, these modified PS-DVB resins were poorly extracted small toward polar organic compounds such as alcohols, aldehydes, ketones and carboxylic acids. Consequently, when SPE is carried out in extremely acidic or basic media, reversed-phase polymeric sorbents (generally based on PS-DVB) are used. The PS-DVB has much lower backgrounds due to improvements in manufacturing processes. The PS-DVB was used as an adsorbent material has demonstrated to provide improved recoveries for phenolic compounds as compared to the traditional and more commonly applied C<sub>18</sub> material [17].

Silica based packing materials are widely used in high performance liquid chromatography (HPLC) because of their mechanical stability and wide variety of derivatizations, as well as their relatively higher column efficiency. Unfortunately, silica based supports also possess a series of drawbacks. One is their inherent low chemical stability at pH above 8 and below 2. This drawback can cause dissolution of the silica support and loss of the bonded phase. In general, ideal ion-exchange packing materials for HPLC are mechanically stable, chemically inert, hydrophilic with no irreversible adsorption, and highly efficient. To overcome the stability problem of silica, researchers have turned their attention to polymeric supports. PS-DVB-based supports have been studied and utilized the most, due to their chemical stability in both strong base and acid. Recently, HPLC ion exchange stationary phase have been developed from the PS-DVB matrix by applying a hydrophilic

coating on the surface. However, the column efficiency could not match that of most silica-based column [18]. It is of interest, therefore, to explore new techniques to treat the surface of PS-DVB beads in order to obtain more variable adsorbent.

### **1.3 Aim and Objectives**

#### **1.3.1 Aim of Sesearch**

The aim of this research is to develop a new chemically modified PS-DVB resin by introducing octadecyloxy group ( $C_{18}H_{37}-O-$ ) onto the PS-DVB backbone. The new modified PS-DVB is compared with unmodified PS-DVB and other modified PS-DVB and these phases are applied as adsorbents in solid phase extraction.

#### **1.3.2 Objectives of Project**

The objectives of this research are:

- a) To synthesize PS-DVB adsorbent using suspension polymerization technique.
- b) To produce modified PS-DVB adsorbents by Friedel-Crafts acylation reaction, chloromethylation, and Williamson ether reaction.
- c) To characterize and study the performance of the adsorbents.
- d) To apply the developed modified PS-DVB resins to SPE analysis.

### **1.4 Scope of Sesearch**

The following are the scopes of sesearch:

- a. Preparation PS-DVB and modification of PS-DVB via
  - i. Friedel-Crafts acylation
  - ii. Chloromethylation
  - iii. Williamson ether reaction

- b. Study of the physical characteristics of PS-DVB and modified PS-DVB by using:
  - i. Fourier transform infrared spectrophotometry (FTIR)
  - ii. Scanning electron microscopy (SEM)
  - iii. Thermogravimetric analysis (TGA)
  - iv. Nitrogen adsorption analysis (NA)
- c. Study of the chemical characteristics of PS-DVB and modified PS-DVB by using:
  - i. Solid phase extraction (SPE)
  - ii. Gas chromatography (GC)

## **1.5 Outline of the Project Report**

This project report consists of six chapters. Chapter 1 presents general background of this research, research aim, research objectives and scope. Chapter 2 compiles the literature reviews and theoretical background on PS-DVB, modification of PS-DVB and its application as an adsorbent for chemical analysis. The procedures for characterization and application of the synthesized materials are presented in Chapter 3. Chapter 4 reports the results and discusses the preparation of PS-DVB, and modified PS-DVB. Chapter 5 describes the characterization and application of unmodified and modified PS-DVB as an adsorbent in the chromatographic analysis. The concluding Chapter 6 summarizes this project report by presenting the overall conclusions and suggestions for future research.



## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Free Radical Polymerization**

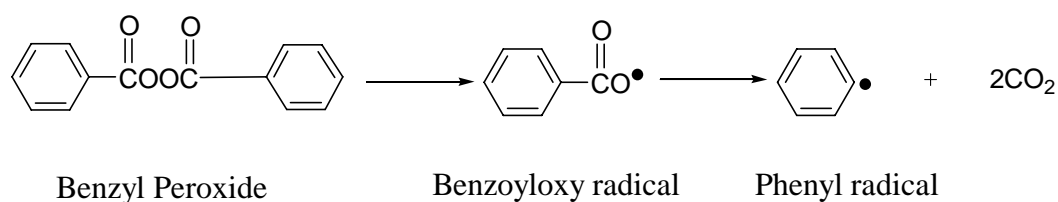
One of the most common and useful reactions for making polymers is the free radical polymerization. It is used to make polymers from vinyl monomers, that is, from small molecules containing carbon-carbon double bonds. Free radical polymerization reactions are of enormous importance in technology. The monomers of these reactions are available in large quantities from the photochemical industry, and the polymers obtained from these monomers form the foundation of much of the polymer industry as explained by Allcock *et al* [19].

The polymerization reactions used in this project are based on free radical polymerization. It consists of three basic steps: initiation, propagation, and termination. In the initiation step, radicals are needed to begin the development of the polymer chain. In the propagation step, free radicals are added to monomer units. The polymer chain will then begin to form with the addition of one monomer unit at a time. The reaction is a very rapid process, and it has been calculated that approximately 1500 monomer units will attach to form a polymer chain in one second. The termination step of free radical polymerization stops a free radical in one of three ways. First, coupling termination; this can be found between free radical

styrene molecules. Second, disproportionation; it is the conjunction of two polymer chains. One of the polymer chains is saturated and the other is unsaturated; both fuse by transfer of hydrogen radical to form a single polymer unit. The third step, termination sequence that consists of a combination of both coupling and disproportionation reactions [12].

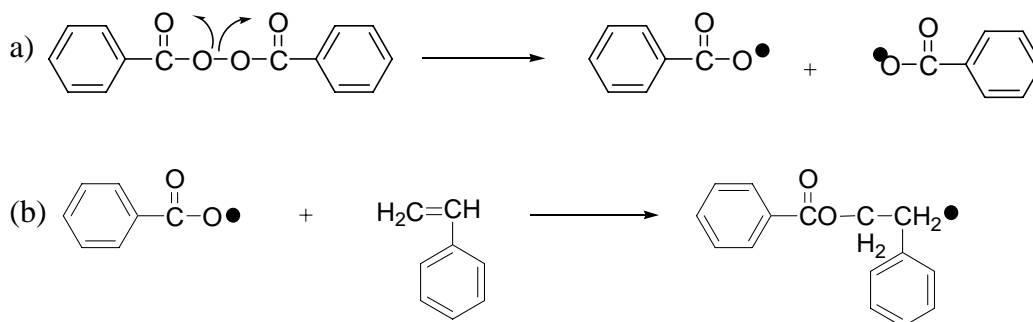
### 2.1.1 Initiation

The initiation of a free radical chain takes place by addition of a free radical ( $R\cdot$ ) to a vinyl molecule. Free radical initiation can occur through application of heat (thermal), photochemical, and ionization. Peroxides such as benzoyl peroxide (BPO), require temperatures in the range of 40-60°C for decomposition and free radical formation [20]. The decomposition of BPO to form radicals is given in Figure 2.1.



**Figure 2.1** Scheme of the Decomposition of BPO to Form Radicals [20]

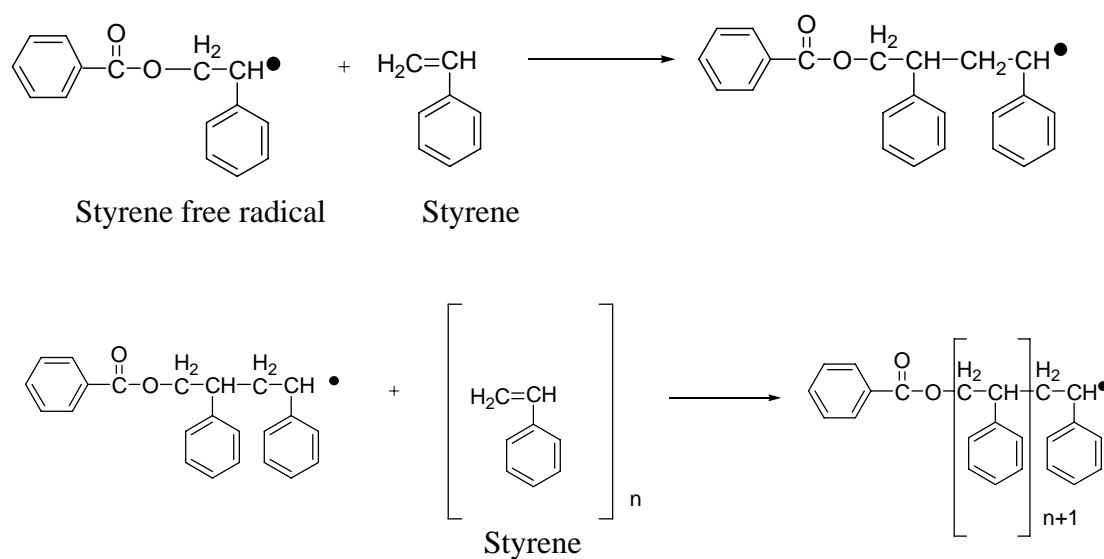
The free benzoyl peroxide radical can react with a styrene unit to initiate the polymerization reaction (Figure 2.2). It is important to note that the free radical ( $R\cdot$ ) is a companion of all polymerizing species and hence should not be called a catalyst, even though it is often referred to as such.



**Figure 2.2** (a) Dissociation of Initiator, and (b) Initiation of Free Radical Styrene Polymerization [19, 20]

### 2.1.2 Propagation

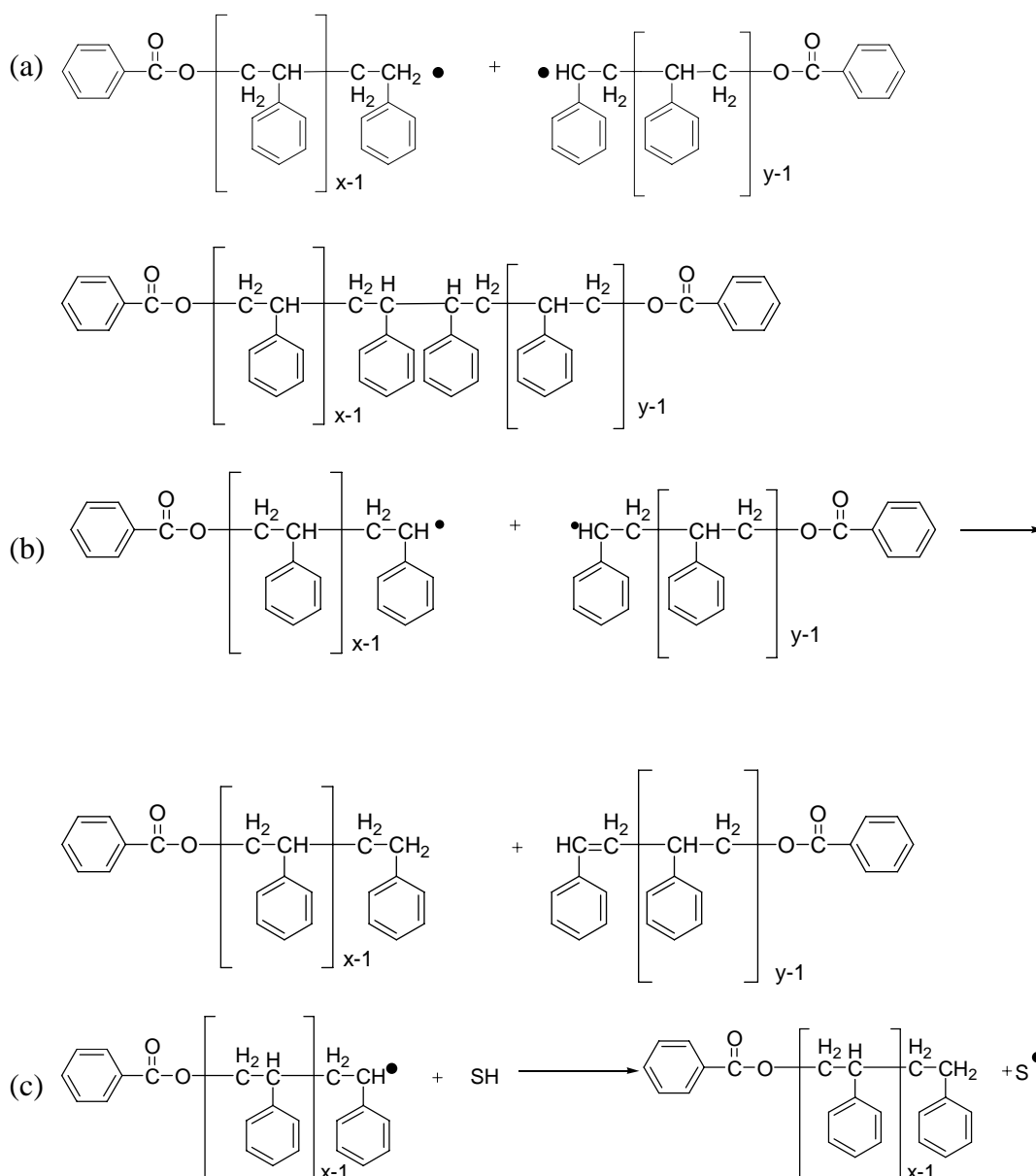
Propagation is a bimolecular reaction, which takes place by addition of the new free radical to another styrene molecule, and by many repetitions of this step, (See Figure 2.3).



**Figure 2.3** Propagation of Free Radical Styrene Polymerization [19, 20]

### 2.1.3 Termination

The termination of the growing free radical chains usually takes place by coupling of two macroradicals. Termination of free radical chain polymerization may also take place by disproportionation. This termination process involves chain transfer of a hydrogen atom from one chain end to the free radical chain end of another growing chain, resulting in one of the 'dead' polymers having an unsaturated chain end [19, 20]. The mechanism of termination is illustrated in Figure 2.4.



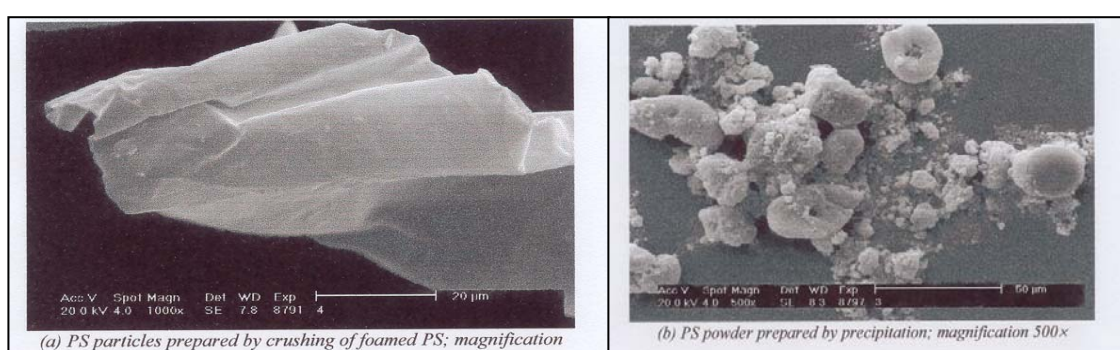
**Figure 2.4** Terminations of Free Radical Styrene Polymerization; by (a) Coupling / Combination, (b) Disproportionation, (c) Chain Transfer [19, 21].

## 2.2 Suspension Polymerization

Hoffman and Delbruch were the first to develop suspension polymerization in 1909 [21]. In suspension polymerization the initiator is soluble in the monomer phase, which is dispersed by comminuting into the dispersion medium (usually water) to form droplets. The solubility of the dispersed monomer (droplet) phase and also the resultant polymer in the dispersion medium are usually low. The volume fraction of the monomer phase is usually within the range 0.1-0.5 mL. Polymerization reactions may be performed at lower monomer volume fractions, but are not usually economically viable. At higher volume fractions, the concentration of continuous phase may be insufficient to fill the space between droplets. Polymerization proceeds in the droplet phase and in most cases occur by a free radical mechanism. Suspension polymerization usually requires the addition of small amounts of a stabilizer to hinder coalescence and break-up of droplets during polymerization. Suspension polymerization is a polymerization process in which the monomer, or mixture of monomers, is dispersed by mechanical agitation in a liquid phase, usually water, in which the monomer droplets are polymerized while they are dispersed by continuous agitation. This process is used for polymerization of PS-DVB where styrene is dispersed in fine droplets into water [22-23].

The free radical initiators are exclusively organic peroxides that need to be soluble in styrene and insoluble in water. The size of the droplets can be adjusted by numerous parameters such as addition of colloids, stirring conditions, reactor geometry, etc. Only organic peroxides initiate suspension polymerization. If the monomer is insoluble in water, bulk polymerization can be carried out in suspended droplets, i.e. monomer is mechanically dispersed. The water phase becomes the heat transfer medium. Since it is a continuous phase, viscosity changes are very little as the monomer converts to polymer, so the heat transfer is very good. In this system, the monomer must be either insoluble in water or only slightly soluble in water, so that when it polymerizes it becomes insoluble in water. The two differences between emulsion and suspension polymerization are [23-24]: (a) the suspension polymerization is a mechanical process, and must have a stabilizing agent until the droplets are far apart, and (b) the emulsion polymerization is a chemical process which requires a surfactant to make the monomer “emulsify”.

The size of the spherical beads formed by the suspension polymerization of styrene ranges from 250 to 450  $\mu\text{m}$  and the average size of milled PS beads was approximately 100  $\mu\text{m}$ . The shape of particles obtained by milling beads under decreased temperature was highly irregular and thermoplastic change was observed on the surface. The size of the PS particles formed by crushing of foamed PS (Fig.2.5a) is also about 100  $\mu\text{m}$ ; the deformed sheet-like shape of crushed foamed PS particles is observed. The particles of PS powder (Fig.2.5b) prepared by precipitation, occur as strongly deformed beads with broad distribution of sizes, which range from approximately 5 to 30  $\mu\text{m}$  [25].



(a) PS particle; magnification 1000  $\times$       (b) PS powder; magnification 500  $\times$

**Figure 2.5** (a) Polystyrene Particle, and (b) Polystyrene Powder [25]

Arshady [26] clarified that beaded copolymers of styrene and divinylbenzene are widely used for the manufacture of strongly acidic and strongly basic ion-exchange resins. Commercially important polystyrene ion exchangers are produced in one or two steps. A variety of related chelating agents can also be produced from the chloromethylated polystyrene by processes basically similar to that of ammonium resins. In suspension copolymerization of activated acrylates with styrene, the monomer solution is dispersed in an aqueous medium to form a microdroplet suspension. Polymerization is then effected at the desired temperature (ca. 60-80°C), to convert the monomer microdroplets to the corresponding polymer microspheres (beads or pearls) [11].

Buchmeiser [27] described a set-up of suspension polymerization that consists of monomer cross-linker droplets that are suspended in a polymerization

medium. For suspension polymerization, there are two phases, water and organic (oil), and the starting point may be 10 parts of the former and 1 part of the latter (v/v). The initiator used can be water-soluble or organic-soluble (benzoyl peroxide, 2,2'-azo-bis-isobutyryl nitrile (AIBN) ) but organic-soluble initiators are more often used.

Suspension polymerization probably remains the most widely practiced method of producing polystyrene. The advantage of suspension process over mass processes is the excellent temperature control that can be obtained through the suspending medium, water. This allows for rapid heat removal and shorter polymerization times. The separation is much easier than in solution polymerization. [21, 23].

Suspension polymerization is extensively employed. Styrene, methyl methacrylate, vinyl chloride, and vinyl acetate are polymerized by suspension process. The process is also referred to as bead, pearl, or granular polymerization because of the forms in which the final products may be obtained. The monomer is dispersed as droplets in water. The monomer droplet size is maintained by mechanical agitation and the addition of stabilizers. Various types of stabilizers are used to prevent agglomeration of the monomer droplets. A protective colloidal agent, often poly (vinyl alcohol) (PVA), is added to prevent coalescence of the droplets. The initiators used are soluble in the monomer droplets. Each monomer droplet is considered to be a small bulk polymerization system. Heat control in suspension polymerization is relatively easy. However, near the end, the particles become hard and are recovered by filtration. Because the liquid is water-based, solvent recovery and treatment problems are minimal. The product usually must be washed, dried, and freed of additives [22, 24].

Arshady [26] explained that the most important feature of organic (oil)/water suspension polymerization is the formation of a droplet suspension of the monomer in water (the suspension medium) and the maintenance of the individual droplets throughout the polymerization process. Droplet formation in an organic (oil)-water mixture is most appropriately accomplished by mechanical stirring, although other forms of mixing can also be employed. By suspension polymerization, the

copolymers produced are in beaded form. It was found that different diluents generated formation of uniform polymer networks with an in-homogeneity mostly related to the kind and amount of inert diluents used

### 2.2.1 Types of Pores

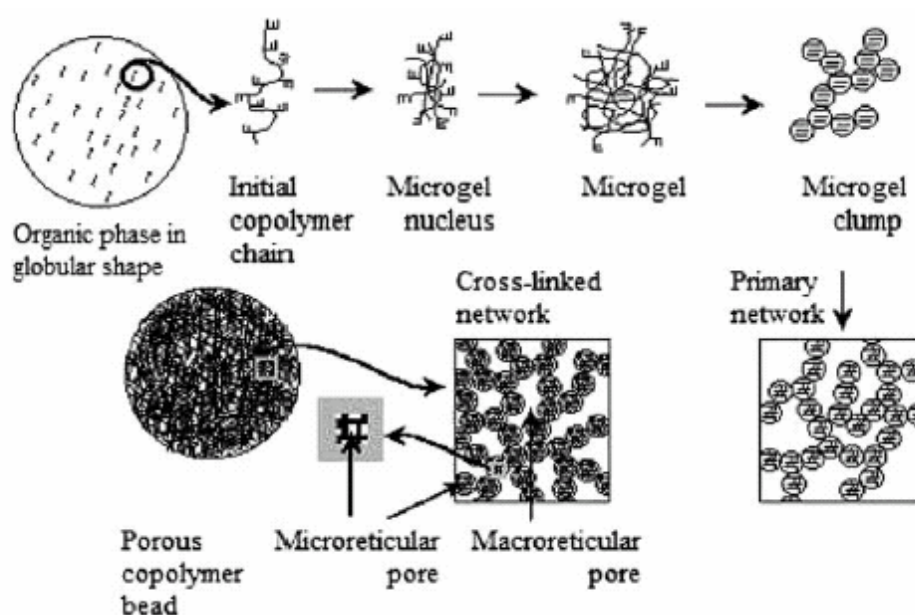
Porosity and surface area in both inorganic and organic supports can be controlled easily during production. For organic resins, gelation and/or precipitation processes that take place during the conversion of liquid micro droplets to solid micro beads determine porosity. For example, polystyrene beads produced in the presence of 1-2% divinylbenzene (DVB) without a monomer diluent have a very low surface area ( $<1 \text{ m}^2/\text{g}$ ) with no real porosity or very small pores. However, by using higher DVB concentrations and a monomer diluent, polymer beads with wide range of porosities can be produced, depending on the proportions of DVB and monomer diluent.

Solid material commonly contains one or more groups of pores, whose size and volume depend on preparation method. The pores are classified into different classes depending on their size [28]:

- Micropores (size  $< 2 \text{ nm}$ )
- Mesopores ( $2 \text{ nm} < \text{size} < 50 \text{ nm}$ )
- Macropores (size  $> 50 \text{ nm}$ )

Matrix porosity is the basis of support characteristics in chromatography, and determines the fraction range of the support. Resin porosity may also affect the support performance in other applications such as affinity chromatography, and solid-phase synthesis. The specific pore volume and pore size distribution in the swollen state may be substantially different from those measured in the dry state [29]. Figure 2.6 illustrates the formation of porous structure of PS-DVB.





**Figure 2.6** Mechanism of Porous Structure Formation during Suspension Copolymerization of Styrene-Divinylbenzene [29]

Based on Figure 2.6, the polymerization reaction takes place in a suspended droplet during oil/water suspension polymerization. As the reaction progresses the copolymer precipitates within the droplet and form spherical shapes called nuclei. The nuclei grow into microspheres (also called microgel) and the microspheres agglomerate with each other resulting in the primary network. Upon further polymerization and cross-linkage, the primary network becomes the cross-linked porous network [29].

### 2.3 Poly (styrene-divinylbenzene)

Poly (styrene-divinylbenzene) (PS-DVB) beads have been used for separations since 1964 when Moore synthesized porous crosslinked polystyrene. Although these rigid PS-DVB matrices can be operated under high pressures without collapsing, they cannot be used directly to purify proteins as the material is difficult

to derivatise with affinity ligands and hydrophobic interactions between the matrix and protein often result in irreversible adsorption or loss yield. The recent trend towards modification of PS-DVB with hydrophilic groups to mask its hydrophobic surface aimed at improving its use in protein chromatography has produced both covalently bonded carboxylic groups and adsorbed hydrophilic groups [30].


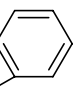
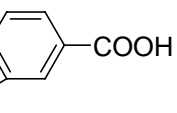
In the course of polymerization, initially homogeneous mixture of reaction components separates into two phases, one of which is cross-linked polymer and the other pure diluents [18]. The densely cross-linked regions in copolymers do not collapse entirely, with the removal of the inert diluents after polymerization and part of the volume, which primarily contained the diluents, appears as pores. Layadene *et al.* [2] have found that the use of precipitant diluents in the preparation of porous styrene-divinylbenzene copolymers give low specific surface area and high porous volume copolymer beads. The porous structure formation has been attributed to phase separation of the copolymer formed during the polymerization process. The selection of diluents as a precipitant is important in determining the porous structure of the polymer beads. For many applications, the presence of meso- and/or macropores is a key requirement to minimize diffusional limitations.

Coutinho *et al.* [1] put in plain words that when styrene-divinylbenzene are copolymerized by a suspension process in the presence of a good solvent for the polymer chains (good diluents), two kinds of porous structures can be obtained: gel or macroporous. At low DVB content the final structure is an expanded gel. When the DVB content and dilution degree are high, a macroporous copolymer is obtained. On the other hand, when the diluents are a poor solvent for the polymer chains (bad diluents), phase separation during the polymerization process takes place and is responsible for the formation of macroporous structures. When mixtures of good and bad diluents are used the copolymers present a porous structure with intermediary characteristic in relation to the copolymers prepared with the pure diluents.

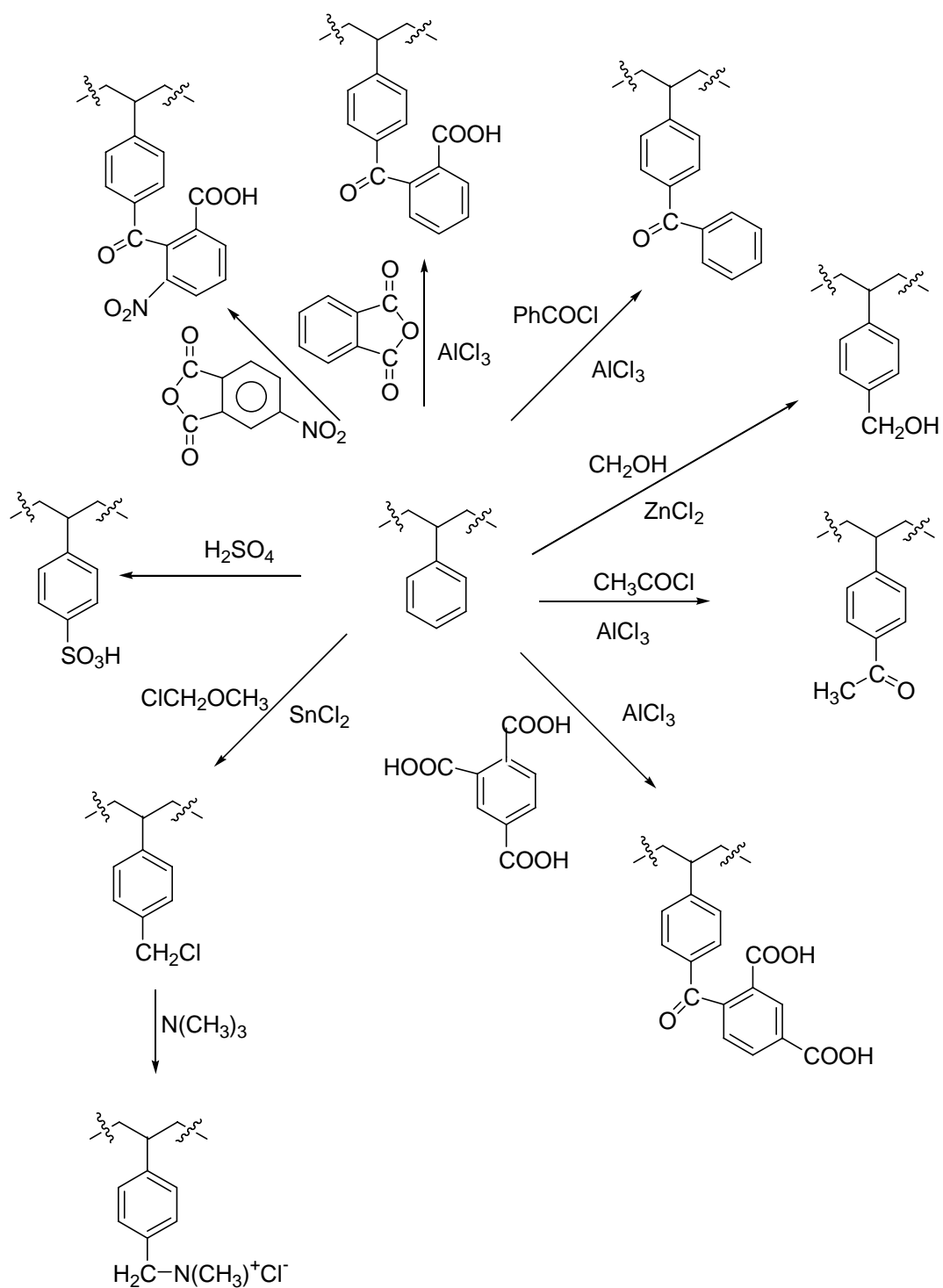
### 2.3.1. Chemical Modification of PS-DVB Resin

Poly (styrene-divinylbenzene) has greater analyte retention, mainly for polar compounds, than bonded silica because their hydrophobic surface contains a relatively larger number of active aromatic sites that allow  $\pi$ - $\pi$  interactions. Nevertheless, sorbents based on PS-DVB have some drawbacks, such as their lack of selectivity and low breakthrough volumes for highly polar compounds, which leads to their incomplete extraction from predominantly aqueous samples. These drawbacks can be largely overcome by using modified resins obtained by attaching polar groups to the aromatic ring on the PS-DVB. These groups are listed in Table 2.1.

**Table 2.1:** Modifiers of the PS-DVB [3]

Group	Structure
Acetyl	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—CH}_3$
Hydroxymethyl	$\text{—CH}_2\text{OH}$
Benzoyl	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$ 
2,4-Dicarboxylbenzoyl	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$ 
<i>o</i> -Carboxybenzoyl	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$ 
sulfonate	$\text{—SO}_3^-$
Trimethylammonium	$\text{—CH}_2\text{—N}(\text{CH}_3)_3^+$

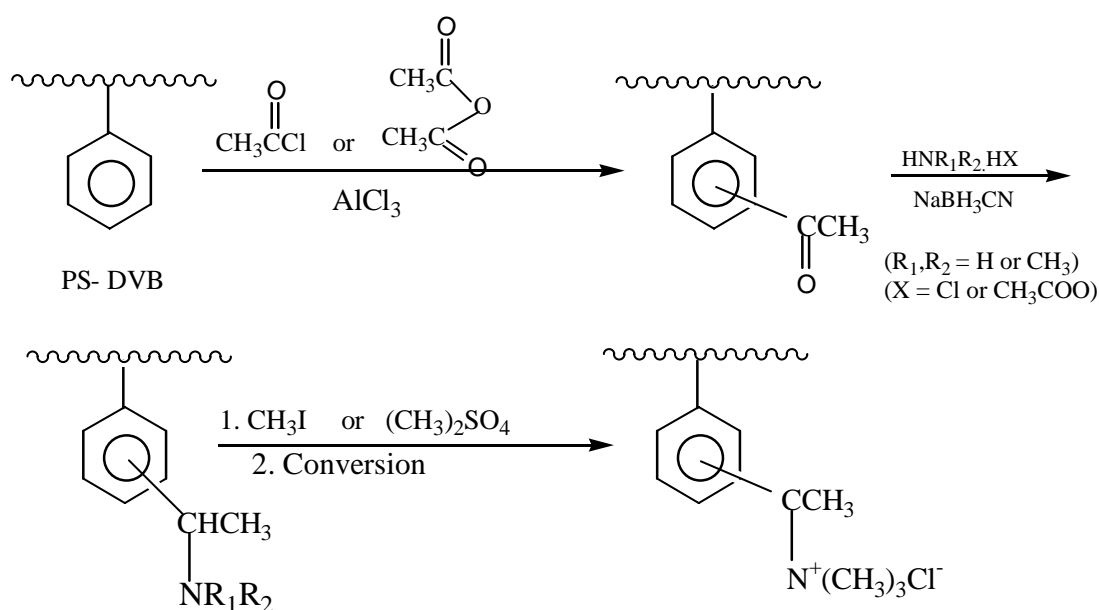
The Figure 2.7 shows examples of PS-DVB modifications in order to achieve higher capacities or a broader and controllable functional variety. Modification of PS-DVB resin to acetyl (a), hydroxymethyl (b) or benzoyl derivatives can be carried out via electrophilic aromatic substitution reaction [3]



**Figure 2.7** Examples of PS-DVB Modifications [3]

Poinescu *et al.* [31] have developed macroreticular network synthesis based on the styrene-divinylbenzene copolymers. There has been increasing interest in using such materials as chromatographic packing supports or porous starting structure for the ion exchangers. Styrene copolymerized with a small amount of DVB results in gel-type copolymers, which are characterized by a swollen state porosity. The modification of PS-DVB by two chemical groups, acetyl and benzoyl, and retained more polar compounds than the unmodified resin.

Sulfonated PS-DVB polymers have been used for many years in ion-exchange chromatography of cations, as well as other analytes [32]. Chlorosulfonated porous PS-DVB copolymers are commonly used as intermediates for the preparation of functional polymers, supported reagents, generally in the form of spherical particles with a size distribution between 0.3 and 0.9 mm [33]. These materials are prepared by free radical suspension polymerization of styrene and divinylbenzene monomers mixture in the presence of a porogeneous agent. A synthetic route for anion exchangers based on cross-linked polystyrene is shown in Figure 2.8.



**Figure 2.8** A Synthetic Route for Anion Exchangers Cross-linked PS-DVB [34]

Masque *et al.* [5] have described the application of chemically modified resin obtained from porous cross-linked PS-DVB phase in the determination of phenolic compounds in water. The PS-DVB resin was chemically modified by two chemical groups (acetyl and benzoyl), retained more polar compounds than the unmodified resin. The unmodified PS-DVB matrix has a total pore volume of  $0.69 \text{ cm}^3/\text{g}$ , and this volume drops to around  $0.4 \text{ cm}^3/\text{g}$  for all the modified matrices. Bacquet *et al.* [35] described the chlorosulfonation of styrene-divinylbenzene copolymer characterized by a modification of the textural parameters. The copolymer specific surface area was initially low, and on chlorosulfonation treatment, decrease to a value of  $1 \text{ m}^2/\text{g}$ , characteristic of unswollen gel type resins. However, no effect of the chlorosulfonation on the porous volume and particles mean diameter was observed with varying reaction parameters.

Xu and Xizhang [34] described the application of Friedel-Crafts reaction on cross-linked polystyrene to prepare acetylated cross-linked polystyrene. The general procedure is as follows: cross-linked polystyrene, swollen in suitable solvent is related with acetyl chloride or acetic anhydride in the presence of anhydrous aluminum, stannic or zinc chloride as catalyst to yield acetylated product. The solvents could be carbon disulfide, nitrobenzene, dichloromethane, and dichloroethane. These solutions are not only good swelling agents for cross-linked polystyrene, but also good carriers of Friedel-Crafts catalysts.

Aromatic rings undergo two types of Friedel-Crafts reactions, alkylations and acylations. Of the two types, acylations are more selective and versatile because they do not give multiple acylation products nor products with rearranged acyl groups as alkylations are prone to do. Friedel-Crafts acylations require the presence of a stoichiometric amount of a Lewis acid, whereas alkylations require the presence of only a catalytic amount of a Lewis acid. This difference is the result of the formation of a complex between the Lewis acid and the carbonyl group of the ketone produced in the acylation. The Friedel-Crafts acylation is the most important method of synthesis for aromatic-aliphatic ketones. The acylation reaction is better than alkylation because once formed, the acylium ion does not rearrange, thus giving unrearranged substitution product [36]. Figure 2.9 shows the step mechanism of acylation reaction of benzene.

**Step 1:**

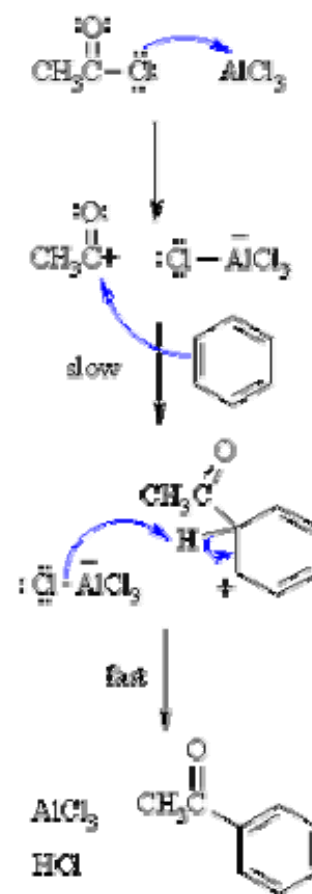
The acyl halide reacts with the Lewis acid to form a more electrophilic C, an acylium ion

**Step 2:**

The  $\pi$  electrons of the aromatic  $C=C$  act as a nucleophile, attacking the electrophilic  $C^+$ . This step destroys the aromaticity giving the cyclohexadienyl cation intermediate.

**Step 3:**

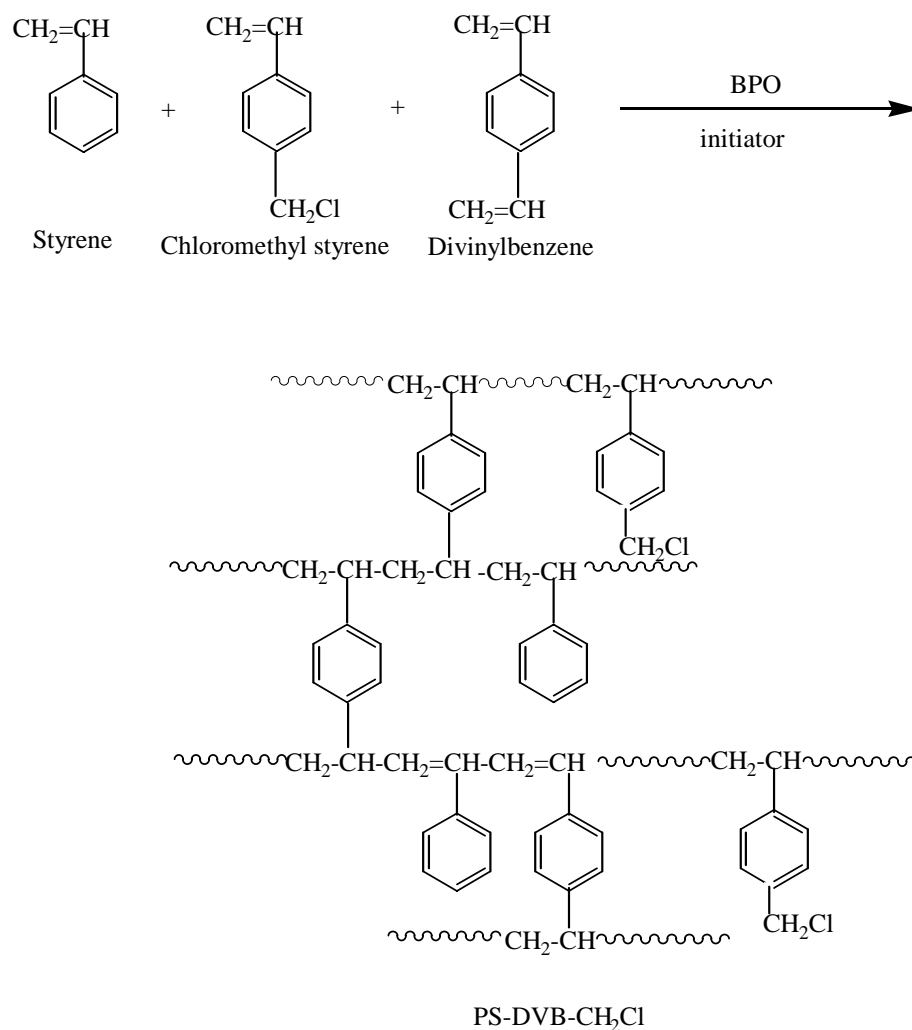
Removal of the proton from the  $sp^3$  C bearing the acyl- group reforms the  $C=C$  and the aromatic system, generating HCl and regenerating the active catalyst.



**Figure 2.9** The Mechanism for the Friedel-Crafts Acylation of Benzene [36]

Chloromethylation is probably the most frequently used method to functionalize styrene-divinylbenzene resins. During chloromethylation of cross-linked macroporous resins, side reactions can occur. These reactions take place with pendent vinyl groups that do not polymerize during the preparation. Indeed, it has been observed that these double bonds will partly disappear during the chloromethylation procedure. During the chloromethylation reaction, the vinyl groups were transformed into unreactive chlorine-containing groups. Instead of the usual method of chloromethylation of cross-linked polystyrene, styrene, chloromethyl styrene, and divinyl benzene is copolymerize to avoid use of the cancer suspect agent chloromethyl methyl ether. The main crosslinking reaction starts with grafting of the crosslinking agent to the polymer backbone. The remaining

chloromethyl group can react with a styrene unit of the polymer chain [37-38]. Figure 2.10 shows a mechanism of chloromethylation of PS-DVB.

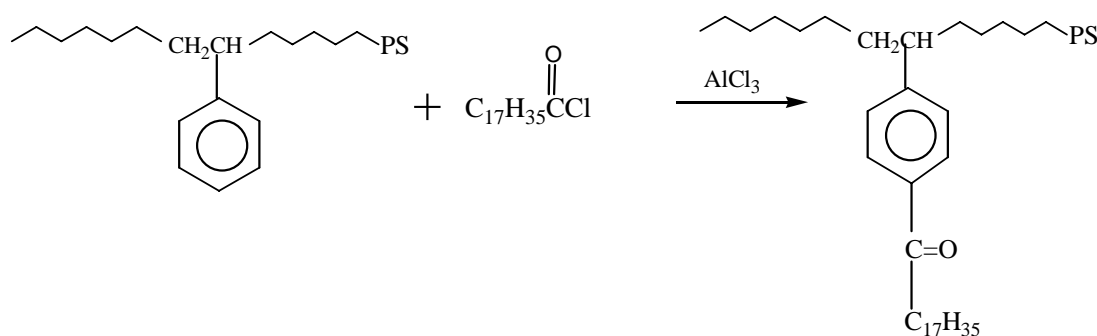


**Figure 2.10** The Reaction of Chloromethylation of PS-DVB

Dumont and Fritz [39] have shown that the modification of a XAD-4 and a spherical PS-DVB resin by incorporating different functional groups into the polymer has a major effect on the retention activities of various analytes. More hydrophobic resins have been prepared by the Friedel-Crafts reaction of different alkylchlorides with the benzene ring of the polymer. In a way, the type of functional group incorporated in the resin can control the hydrophobicity of the resin. In contrast to the resin described in the present work, most of the commercially available polymeric supports for HPLC are generally prepared by suspension polymerization followed by a size classification procedure.



Acylation allows a variety of functionalization to be achieved. These transformations are normally carried out easily from an acylating agent by means of the Friedel-Crafts reaction using nitrobenzene as the solvent and aluminum chloride as the catalyst. In a previous work carried out in the laboratory [40], the stearyl chloride as an acylating agent was prepared by conversion of stearic acids with thionyl chloride,  $\text{SOCl}_2$ . The stearyl chloride was further used in Friedel-Crafts acylation (Figure 2.11).



**Figure 2.11** Preparation of Modified PS-DVB by Using Stearyl Chloride [40]

The reaction progresses rapidly, usually requiring no more than 2 hours. It was experienced that for reaction times greater than 2 hours, decomposition or degradation occurred and the total yield markedly decreased. Also it is notable that the reaction should be performed at ambient temperature to protect the resin from over swelling and correspondingly crushing [41].

## 2.4. Application of Modified PS-DVB Resin

Dominic and Howard [42] explained that the polystyrene-divinylbenzene matrices have been used in chromatography for many years and these matrices can be operated under high pressures without compression. Chemically modified PS-DVB resins have also been developed and used in the SPE of polar compounds mainly from aqueous samples. Masque and Galia [43] described the synthesis and

SPE application of a new chemically modified PS-DVB resin for the analysis of pesticides and phenolic compounds in environmental waters.

A wide range of organic compounds in drinking and surface water could be adsorbed on a hydroxylated PS-DVB cartridge and then eluted with acetone ethyl acetate. If the hydroxylated PS-DVB cartridges were eluted with toluene; the polar interactions were strong enough to retain phthalic acid and monoesters while the diesters were smoothly desorbed [13].

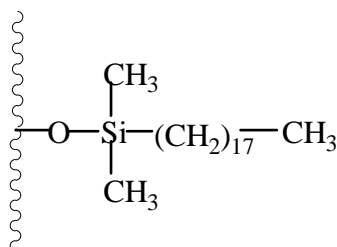
The use of PS-DVB polymers as an adsorbent material has been demonstrated to provide improved recoveries for phenolic compounds as compared to the traditional and more commonly applied C<sub>18</sub> material [44]. Fritz and Schmidt shown that [45] modified porous polystyrene-divinylbenzene resins containing polar groups are superior for SPE of organic solutes from aqueous samples.

Smigol and Svec [46] reported pore-size specific functionalizations for the separation of proteins and small hydrocarbons. For that purpose, large polymer pores were provided with phenyl groups in the presence of hydrophilic groups. In contrast, small pores were provided with much higher phenyl content.

Since porous polystyrene resins have hydrophobic surface, Sun and Fritz [47] have proposed the insertion of an acetyl or hydroxymethyl group into porous PS-DVB to provide a more hydrophilic surface, which can be easily wetted by water alone. Schmidt *et al.* [48] explored the result obtained when acetyl-PS-DVB resins are incorporated into SPE membranes, using them to extract phenols from water. Powell [44] has studied hydroxymethyl-or-acetyl-PS-DVB for preconcentration of pollutant compounds. It was found that acetyl resin retained triazines such as atrazine better than the hydroxymethyl modified material, but recovery of phenol was very poor.

## 2.5. Octadecyl Silane Bonded Silica (C<sub>18</sub>-silica)

Silica based stationary phases remain, after several decades of development, the first choice for most separations. Silica has several limitations. It has low thermal and pH stability, and the silanol activity of the specific phase must be considered when a silica-based column is used for the separation of basic analytes. The silanol activity of a silica-based column originates in the accessible residual silanol groups present on the surface even after it is chemically modified. The Figure 2.12 shows the structure of the octadecyl silane-silica [49].



**Figure 2.12** The Structure of Octadecyl Silane-Silica

C<sub>18</sub>-silica is a non-polar SPE sorbent that contains octadecyl (C<sub>18</sub>) functional groups bonded to the surface of silica that alter their retentive properties. Modified silica with C<sub>18</sub> reversed-phase sorbent is one of the most widely used packing materials for SPE because of its greater capacity compared to other bonded silica, such as the C<sub>8</sub> and CN types [3]. The mechanisms of retention are based on hydrophobic interactions between the solutes and the stationary phase (Van der Waals forces) and on secondary interactions such as hydrogen bonding and dipole-dipole forces (hydrophilic or polar interactions) [3, 51, 52]. C<sub>18</sub>-silica has a non-polar characteristic due to the octadecyl groups on the surface and the silanol groups present allows the polar and ionic secondary interactions between the adsorbent and the solutes [53].

Numerous applications report the use of C<sub>18</sub>-silica, as indicated by the studies reported for water. In particular, organometallic compounds can be retained on this sorbent due to possible hydrophobic interactions. Bare C<sub>18</sub>-silica can also retain a fraction of inorganic trace elements, probably due to the presence of silanol groups on its surface [50].

## 2.6. Materials and Methods for Solid-Phase Extraction (SPE)

Solid-phase extraction (SPE) with porous solid particles goes back to the early 1970's. However, SPE has become more popular recently due the need to replace liquid extraction procedures, which use large quantities of organic solvents. Considerable attention is now being paid to solid-phase extraction (SPE) as a way to isolate and preconcentrate desired components from a sample matrix. In addition to being fast, efficient and easily automated, SPE is a clean analytical procedure. In SPE the extractant is a porous, particulate solid which has a large surface area available for interaction with the liquid sample solution [54].

Fritz and Masso [55] found that one problem with extraction materials is the inability of aqueous solutions to adequately wet their surface, which is usually hydrophobic. This is true for both C<sub>18</sub>-silica and underivatized polystyrene-divinylbenzene resin. Pretreatment of the resin column or cartridge with methanol is usually necessary to obtain better surface contact with the aqueous solution. Fritz *et al.* [56] explained that SPE is fast and effective, and can provide concentration factors of 100-fold or more. Solid phase extraction has become the preferred technique for sample pre concentration. Being a multistage method, it is more efficient than simple liquid-liquid extraction, more easily automated and much less polluting than liquid extraction techniques that often use relatively large volumes of organic solvent. Very little chemical waste is produced. In general, polymeric sorbents such as PS-DVB retain organic analytes more strongly than silica-based materials.

SPE can be divided into two major categories:

**Type I:** Single-equilibrium methods in which each analyte partitions between a liquid or gaseous sample and a solid extractant. The type I methods often give a lower but fixed percentage extraction. SPE type I methods are usually done on micro scale (solid phase micro extraction, SPME).

**Type II:** Multi-equilibrium methods in which the sample flows through a bed of a solid extractant. Since a typical device may contain 20 or more theoretical plates, retention of analytes is generally more complete than with single-

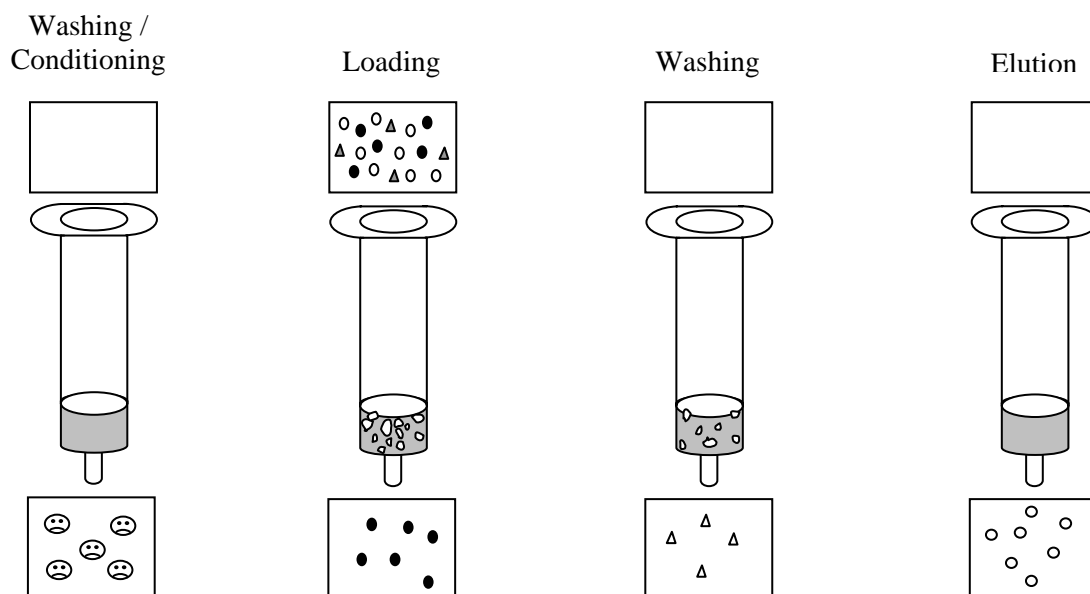
equilibrium methods. Type II methods usually give nearly complete extraction of the desired analytes. A current challenge is to do type II extractions quickly and efficiently on a smaller scale, the bed of solid extractant must also be made smaller [55].

The particle size also needs to be made smaller to speed up the rate of mass transfer of analytes from the liquid samples to the solid extractant. Perhaps the best way to accomplish this is to use a resin-loaded membrane such as the 3M Empore series. However, it is important to have intimate contact between the predominately aqueous samples and the surfaces of the solid extractant particles.

When SPE has to be carried out in extremely acidic or basic media, reversed-phase polymeric sorbents (generally based on PS-DVB) are used. In addition to their broader pH-stability range that increases the flexibility of the methods, these kinds of sorbents have a greater surface area per gram and they show relatively selective for analytes with aromatic ring because of the specific  $\pi$ - $\pi$  interactions. In an attempt to improve the efficiency of SPE procedures, materials based on polymers other than PS-DVB have been tested. One important parameter to be taken into account in SPE is the selectivity of the stationary phases, especially when compounds are to be extracted from complex matrices, since the main objective is to remove interferences prior to the analysis. SPE materials based on silica and polystyrene-divinylbenzene stationary phases are generally non-selective and can lead to difficulties with interference co-extracted. [3].

SPE method always consists of the three to four successive steps, as illustrated in Figure 2.13 [50]. First, the solid sorbent should be conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step is crucial, as it enables the wetting of the packing material and the solvation of the functional groups. The second step is the percolation of the sample through the solid sorbent. Depending on the system used, volumes can range from 1 mL to 1 L. The third step (which is optional) may be the washing of the solid sorbent with an appropriate solvent, having low elution strength, eliminate matrix components that have been retained by the solid sorbent, without displacing the analytes. The final

step is the elution of the analytes of interest by an appropriate solvent, without removing the retained matrix components.



**Figure 2.13** SPE Operation Steps [50, 57]

Polystyrene-based polymers may be an interesting alternative to common sorbents (namely Amberlites XAD-2 and XAD-8,  $C_{18}$ -silica) when they have a hyper cross-link structure [50, 54]. The addition of a reagent to the sample is required to form complexes that are further retained on the hydrophobic sorbent. Despite the numerous steps and parameters used to enable efficient extraction and recovery of the target analytes, the choice of the solid adsorbent is the most critical step.

The breakthrough volume is the most important characteristic parameter to determine the suitability of a sampling device for isolating the analytes of interest. The procedures are different depending on the field of application. In many cases, the handling of biological samples differs from those of environmental samples. The most straightforward is direct method using either on-line or off-line detection. Measurement of breakthrough volume can be performed by monitoring continuously or discretely the UV signal at the outlet of a pre-column or a cartridge [9, 10].

## **CHAPTER 3**

### **METHODOLOGIES**

This chapter discusses about materials and procedures used in the preparation of PS-DVB, and modification of PS-DVB by Friedel-Crafts acylation, chloromethylation, and Williamson ether reaction.

#### **3.1 Materials and Reagents**

The following materials were used in the preparation PS-DVB, and modification of PS-DVB.

##### **Styrene Monomer**

The styrene monomer used in this research was from Fluka Chemika (Switzerland) (99%, stabilized with 0.005% 4-tert-butylcatecol). The styrene monomer was washed consecutively with 10% sodium hydroxide (50 mL  $\times$  3) and distilled water (50 mL  $\times$  3) prior to use.

## **Divinylbenzene**

Technical-grade divinylbenzene (DVB) used as the crosslinker in laboratory grade (70-85%) stabilized with 0.2% 4-*tert*-butylcatecol obtained from Merck (Schuchardt, Germany) and Fluka Chemika. The DVB was purified with 10% sodium hydroxide (50 mL  $\times$  3) and distilled water (50 mL  $\times$  3) before use. The procedure was carried out for each PS-DVB synthesis.

## **Benzoyl Peroxide**

Benzoyl peroxide (BPO) used as initiator for the PS-DVB synthesis was from BDH. The BPO was purified by washing with chloroform and poured into cold methanol and filtered with sintered funnel. The product was stored in a refrigerator at 4°C. The average molecular weight of the BPO used was 130.19 g/mol; its density was 0.919 g/mL.

## **Stabilizers**

Polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) were used as the stabilizer in this work. Each stabilizer was dissolved in distilled water before use. The PVA, with an average molecular weight of 125,000 g/mol was obtained from Merck (Schuchardt, Germany) and Fluka Chemika (Switzerland).

## **Stearoyl chloride**

Stearoyl chloride ( $\text{CH}_3(\text{CH}_2)_{16}\text{COCl}$ ) used in this research has an average molecular weight of 302.93 g/mol, and density of 0.908 g/mL. It was obtained from Merck (Schuchardt, Germany) and Fluka Chemika (Switzerland).

## **Chloromethyl-styrene (4-vinylbenzyl chloride)**

Chloromethyl styrene ( $\text{H}_2\text{C}=\text{CHC}_6\text{H}_4\text{CH}_2\text{Cl}$ ) used in this research has an average molecular weight of 152.62 g/mol, and density of 1.083 g/mL. It was obtained from Merck (Schuchardt, Germany) and Fluka Chemika (Switzerland).



**1-Octadecanol (octadecyl alcohol)**

1-Octadecanol ( $\text{CH}_3(\text{CH}_2)_{17}\text{OH}$ ) used in this research has a molecular weight of 270.50 g/mol, and melting point of 56-58°C. It was obtained from Merck (Schuchardt, Germany) and Fluka Chemika (Switzerland).

**Nitrobenzene**

Nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ) used in this research has an average molecular weight of 123.11 g/mol, and boiling point of 83-84°C. It was obtained from Merck (Schuchardt, Germany).

**2-Chlorophenol**

2-Chlorophenol ( $\text{C}_6\text{H}_5\text{ClO}$ ) used in this research has an average molecular weight of 128.56 g/mol, and boiling point of 62-63°C. It was obtained from Fluka Chemika (Switzerland).

**Methanol**

Methanol used in this research was obtained from Merck (Schuchardt, Germany).

***p*-Cresol**

*p*-Cresol used was technical grade, obtained from Riedel-de-Haën (Switzerland).

**Benzaldehyde**

Benzaldehyde used was technical grade, obtained from Riedel-de-Haën (Switzerland).

## Butyrophenone

Butyrophenone used was technical grade, obtained from Fluka Chemika (Switzerland).

### 3.2 Synthesis

#### 3.2.1 Preparation of PS-DVB and Its Derivatives

The PS-DVB synthesis was carried out in a reactor equipped with a mechanical stirrer, thermometer, nitrogen purge inlet, oil bath and the temperature set at 70°C (Fig.3.1). Poly vinyl alcohol (PVA) (1.0 g) and deionized distilled water (500 mL) were added to the reactor and stirred until dissolution was complete. The above solution was diluted to 500 mL. After the solution temperature reached 70°C (isothermal conditions), the reactor was purged with nitrogen gas. Divinyl benzene (9.6 g), styrene (120 g) (8% by weight) and benzoyl peroxide (1.2 g) were premixed and added to the reactor. The reaction mixture was mechanically stirred for 15 h, and the speed of stirrer was at 900 rpm. It was then filtered off, washed with distilled water and dried. The beads obtained were sieved to separate the 200-400 mesh portions (75-38  $\mu\text{m}$ ). This part was suspended in 10% aqueous solution of HCl (v/v) and stirred for 1 h at 50°C. Then it was filtered, washed with distilled water and dried at 80°C for 12 h. The yield was 129.70 g (99.16%) as white powder; IR  $\nu_{\text{max}}$  (KBr)  $\text{cm}^{-1}$ : 1598.9 (m, C=C aromatic), 751.2 (s, monosubstituted benzene), 696.2 (s, monosubstituted benzene).



**Figure 3.1** Reactor for Polymerization of PS-DVB

### 3.2.2 Friedel-Crafts Acylation of PS-DVB by Using Stearoyl Chloride

Stearoyl chloride (1.10 mL) was dissolved in 1,2-dichloroethane (24 mL) in a round-bottomed flask (250 mL) at room temperature. The temperature of the solution was lowered to 0°C in an ice bath, and purged with nitrogen gas. PS-DVB powder (2.04 g) was gradually added to the above acid chloride solution while stirring magnetically at 0°C. At the end of addition, it was allowed to stir for 30 min at this temperature and then AlCl<sub>3</sub> (1.92 g) portion was added to this mixture. After 60 min of stirring at 0°C, the temperature of the reaction was raised to room temperature. The reaction was carried out overnight. The mixture was then filtered off and the solid was washed according to the following procedure: (i) 10% aqueous solution of HCl (v/v) (5 × 20 mL); (ii) 10% aqueous solution of NaOH (w/v) (5 × 20 mL); and (iii) distilled water (5 × 20 mL). The yield of brown powder was 12.56 g (44.10%); IR  $\nu_{\text{max}}$  (KBr) cm<sup>-1</sup>: 1677.90 (w, C=O stretching), and 1603.7 (w, C=O stretching).

### 3.2.3 Chloromethylation of PS-DVB

The poly vinyl alcohol (PVA) (1.0 g) and deionized distilled water (500 mL) were added to the reactor equipped with a mechanical stirrer, thermometer, nitrogen purge inlet, and oil bath. The temperature of the mixture was set at 70°C and stirred until dissolution was completed. After the solution temperature reached 70°C (isothermal conditions), the reactor was purged with nitrogen gas. Divinyl benzene (12.16 mL), styrene (69.12 mL), chloromethyl styrene (24.20 mL) and benzoyl peroxide (1.2 g) were premixed and added to the reactor. The reaction mixture was mechanically stirred for 15 h, and the speed of stirrer was 900 rpm. The mixture was filtered and the solid was washed with distilled water and dried at 80°C for 12 h to yield a white powder (74.73 g, 70.85%); IR  $\nu_{\max}$  (KBr)  $\text{cm}^{-1}$ : 758.0 (s, C-Cl stretching), and 698.2 (s, C-Cl stretching).

### 3.2.4 Preparation of Benzyl Hexyl Ether as a Reaction Model

Dried hexanol (25 mL) was placed in a round-bottomed flask (250 mL) fitted with a Liebig-type reflux condenser. Clean sodium (0.575 g) in small pieces was added to hexanol and warmed under reflux until all the sodium has reacted (2 h). The reaction was allowed to proceed overnight, by which time all the sodium will have reacted. Benzyl chloride (5 g) was added to the flask and the mixture brought to reflux gently for 2 h. The crude ether was distilled off and most of the hexanol still present in the crude ether was removed by heating under reflux for 2 h with a large excess of sodium and distilled until no more liquid passes over. The residue was benzyl hexyl ether (3.54 g, 13.32%) in the form of a yellow powder; IR  $\nu_{\max}$  (KBr)  $\text{cm}^{-1}$ : 1614.3 (m, C=C stretching phenyl), 1562.2 (s, C=C aromatic), 1452.3 (s, C=C aromatic), and 1107.1 (w, C-O ether).

### 3.2.5 Preparation of Octadecoxy Methyl PS-DVB (PS-DVB-CH<sub>2</sub>-O-C<sub>18</sub>H<sub>37</sub>)

1-Octadecanol (204 g) in dried toluene (250 mL) was placed in a round-bottomed flask (500 mL) fitted with a Liebig-type reflux condenser and clean sodium (5.75 g) in small pieces was warmed under reflux until all the sodium has reacted (2 h). The reaction was allowed to proceed overnight, by which time all the sodium had reacted. The *p*-chloromethyl PS-DVB (39 g) (20 mL) was distilled to get the crude ether (product). The crude ether was again distilled to remove most of toluene and benzene a large excess of sodium until no more liquid passes over. The PS-DVB-CH<sub>2</sub>-O-C<sub>18</sub>H<sub>37</sub> was collected and excess of CH<sub>3</sub> (CH<sub>2</sub>)<sub>17</sub>ONa was removed by dissolving and heating in toluene. Then the crude ether was filtered, and dried under vacuum. The residue was octadecoxy methyl PS-DVB (2.46 g, 1.23%) g; IR  $\nu_{\text{max}}$  (KBr) cm<sup>-1</sup>: 1562.2 (m, C=C aromatic), 1467.7 (m, C=C aromatic), and 1058.8 (w, C-O ether).

### 3.3 Characterizations

The products obtained in this research were characterized as follows:

A. The Fourier transform infrared (FTIR) spectra of the polymer were recorded with a Shimadzu-8300 spectrometer (Kyoto, Japan) in the range of 4000-400 cm<sup>-1</sup>. Small amounts of potassium bromide (KBr) and polymer samples were mixed with a ground mortar and pestle. The mixture was placed in the mini press, and the screws were tightened to squeeze the KBr and polymer mixture into a thin, semi-transparent disk. The mini-press containing the disks was then placed into FTIR instrument and an infrared laser was passed through the disk at a different wavelengths.

B. The shape and surface texture of the particles have been monitored by observation with a scanning electron microscope (SEM) (Philips XL-40). The sample was done by grinding into fine powder before adhering them onto a flat surfaced of an aluminum sample stub that was stuck with a double-sided carbon tape. The doubled-sided carbon tape was used to eliminate any possible discharged of powder

sample from the surface of the sample stub while scanning was done. The sample studied comprise of commercial sample, thus may need to be coated with gold before SEM investigation. The sprinkled sample was placed in a Bio Rad SEM coating system apparatus to be coated with gold using a gold sputter at  $10^{-1}$  Mbar. The purpose of the coating is to ensure that the sample is able to withstand electron bombardment without causing any charging effect. In order to see the morphology of the sample, a Philip XL40 microscope was used with the energy 15.0 kV couple with EDX analyzer. The sample was bombarded using an electron gun with a tungsten filament under 25kV resolution to get the required magnification image.

C. The pore size and surface area of copolymers samples (specific surface area, in  $\text{m}^2/\text{g}$ ) were determined by BJH (Barrer, Joiyner and Halenda) and BET (Brunauer, Emmet and Teller) methods from low temperature nitrogen adsorption isotherms after degassing at  $60^\circ\text{C}$  / 1. m. Pa for 3 hours on a micromeritic apparatus (ASAP 2010, USA). Micrometrics ASAP 2010 instrument was used for the nitrogen adsorption analysis at temperature  $-196^\circ\text{C}$  (boiling temperature of liquid nitrogen) in order to determine the catalyst surface area and porosity. The sample, weighed at 0.5 g was out gassed at  $120^\circ\text{C}$  for 5 hours and left under vacuum to cool to room temperature before measurement. The adsorption-desorption process was done automatically under nitrogen and took a few hours for the whole process to complete depending on the types of sample.

D. The thermal gravimetric analyzer (TGA) was conducted using a Mettler Toledo Thermal analyzer (TC-15). The TA controller in air was set at a rate of  $12^\circ\text{C}/\text{min}$  within a temperature range of  $100\text{--}800^\circ\text{C}$ . Thermogravimetric analysis (TGA) suspends a sample on a highly sensitive balance over a precisely controlled furnace. Usually heating rates of  $10\text{--}20^\circ\text{C}/\text{min}$  are used to look for broad decomposition stages, while slower heating rates around  $1^\circ\text{C}/\text{min}$  are better for isolating individual events. Decomposition in air indicates the processes, which may occur before ignition, while their absence or delay under nitrogen is indicative of a condensed phase decomposition mechanism. Sample sizes are usually kept as small as possible; within the limits of the apparatus this is usually around 5 mg per run.

### **3.4 Solution Preparations**

#### **3.4.1 Stock Solution Preparation**

Stock solutions of test compounds (100,000 ppm) were prepared by weighing benzaldehyde (2.5 g), butyrophenone (2.5 g), 2-chlorophenol (2.5 g), *p*-cresol (2.5 g) and nitrobenzene (2.5 g) separately in five 25-mL volumetric flasks and each compound was dissolved and diluted in methanol to 25 mL. Butyrophenone was used as the internal standard.

#### **3.4.2 Sample Aqueous Solution Preparation**

The aqueous sample solution for SPE containing individual test compounds were prepared by adding stock solutions (each 100,000 ppm) of benzaldehyde (0.1 mL), *p*-cresol (0.1 mL), 2-chlorophenol (0.1 mL) and nitrobenzene (0.1 mL) into four separate 10-mL volumetric flasks, respectively and each solution was then diluted to 10 mL with deionized water. Thus, the aqueous sample solution prepared contained 1% (v/v) of methanol and the concentrate of each compounds in 1000 ppm. An aqueous solution containing a mixture of the four test compounds were prepared by adding benzaldehyde stock solution (0.1 mL), *p*-cresol stock solution (0.1 mL), 2-chlorophenol stock solution (0.1 mL) and nitrobenzene stock solution (0.1 mL) into a 10 mL volumetric flask and then diluted to the mark with deionized water. Therefore, the solution contained 4% (v/v) of methanol. The concentration of each test compounds in 1000 ppm.

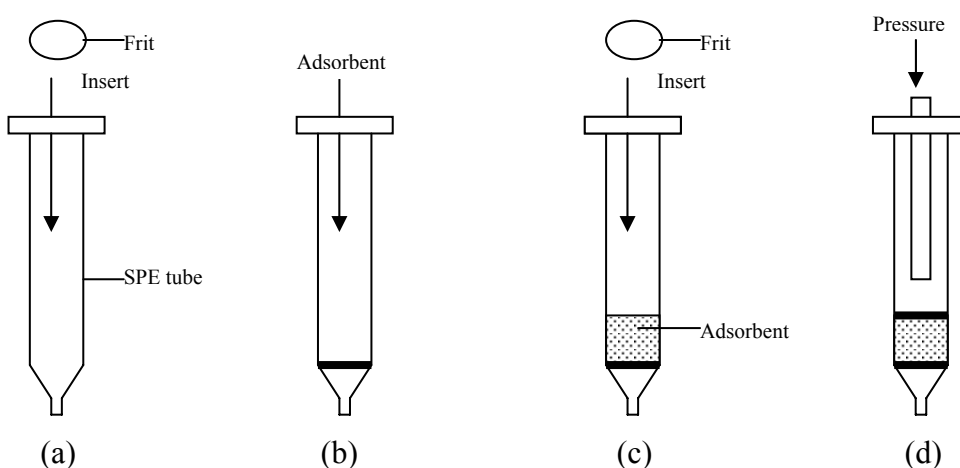
#### **3.4.3 Sample for GC Peak Identification**

For the peak identification purpose, a mixture solution was prepared by adding 0.1 mL of each stock solution into a 5-mL volumetric flask and then diluted to 5 mL with methanol to give 2000 ppm of each compound. 1  $\mu$ L of this mixture was injected into the gas chromatograph.

### 3.5 Solid Phase Extraction

#### 3.5.1 SPE Tube Packing

Four SPE tubes used in this research were packed in the laboratory with four different synthesized adsorbents. They were (i) native PS-DVB, (ii) PS-DVB heptadecyl ketone, (iii) chloromethyl PS-DVB, and (iv) octadecoxy chloromethyl PS-DVB. First, a frit was inserted into an empty 6 mL SPE tube (International Sorbent Technology Limited, UK) until it reached the bottom of the tube. Then 0.5 g of the adsorbent was weighed and added into the tube. Another frit was inserted into the SPE tube so that the adsorbent was placed between the frits. A light pressure was applied on the second frit to obtain a uniform and compact packing of the adsorbent. The SPE tube packing process is illustrated in Figure 3.2.



**Figure 3.2** SPE Tube Packing Process: (a) Inserting the First Frit. (b) Adding 0.5 g of Adsorbent into the Tube. (c) Inserting the Second Frit. (d) Applying Pressure on the Frits and Adsorbent.

#### 3.5.2 Conditioning and Elution of SPE Tube

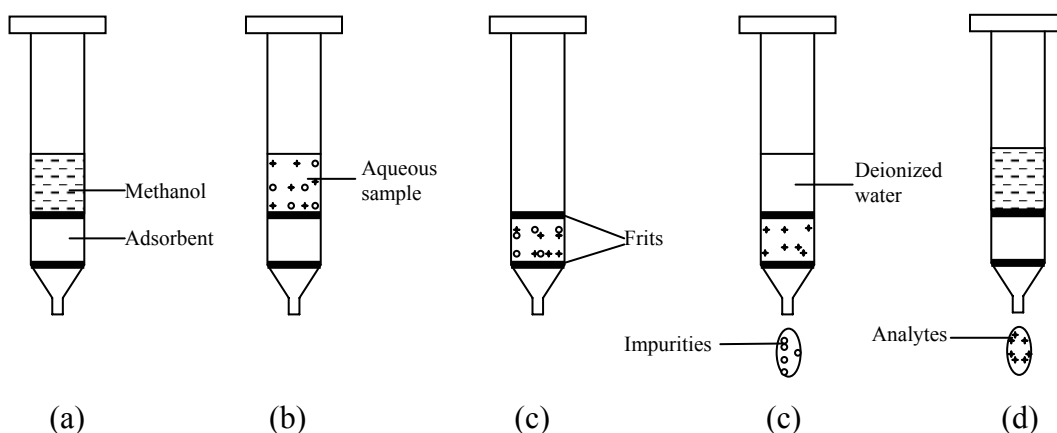
SPE tubes containing home-made adsorbents were tested together with commercial tubes. The commercial SPE tubes used for solid phase extraction were a 6-mL SPE tube pre-packed with 500 mg of C<sub>18</sub>-silica adsorbent. In the SPE procedure, the SPE tubes were mounted onto a 10-port vacuum manifold obtained



from Vac-Master (International Sorbent Technology), connected to an EYELA A-3S Aspirator (Tokyo Rikakikai Co. Limited, Japan). Regulating the air pressure release valve controlled the flow rate of the sample solution.

Five SPE tubes used in this research were (i) C<sub>18</sub>-silica adsorbent, (ii) PS-DVB adsorbent, (iii) PS-DVB heptadecyl ketone adsorbent, (iv) chloromethyl PS-DVB adsorbent, and (v) octadecyloxy methyl PS-DVB. These tubes were connected on a 10-port vacuum manifold that was connected to a water aspirator. Centrifuge tubes were placed beneath the SPE tubes inside the vacuum manifold to collect the eluate.

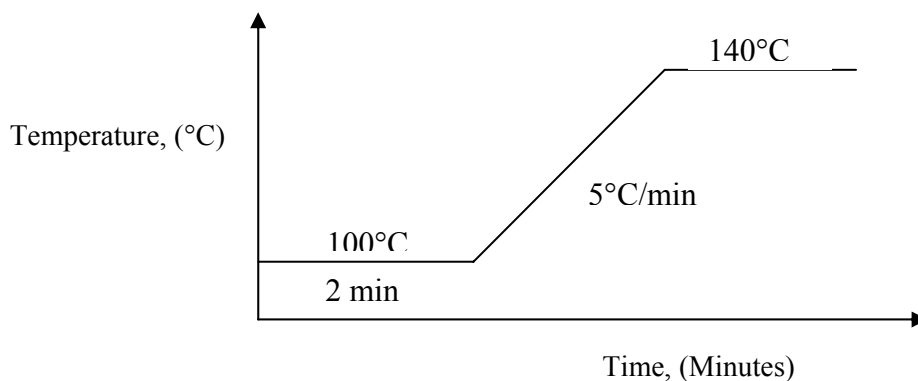
Before use, the SPE tubes were rinsed with 12 mL of methanol to remove impurities, and then dried (by vacuum suction). They were then conditioned with 2 mL of methanol to serve as an “activating” solvent and left to soak for 2 minutes before methanol was drawn off. The aqueous sample solution (10 mL) was sucked through the tube by vacuum manifold, connected by a water aspirator, with the vacuum adjusted to give a flow rate of 1 mL/min. After passage of the aqueous sample, the tube was then rinsed with 2 mL of deionised water to remove impurities and was dried by vacuum suction for a few minutes. Elution was performed with four 1 mL portions of methanol. The eluate was collected into a centrifuge tube. The internal standard (0.05 mL) (butyrophenone) (100,000 ppm) was added into the centrifuge tube and the eluate was made up to 5 mL with methanol. All the eluates were stored in the freezer before injection into the gas chromatography. This SPE process was repeated twice to obtain three replicates runs. Figure 3.3 shows the solid phase extraction process.



**Figure 3.3** Solid Phase Extraction Process: (a) Conditioning with Methanol. (b). Aqueous Sample Filling. (c) Drying. (d) Cleanup with Deionised Water to Remove Impurities. (e) Elution of Analytes with Methanol.

### 3.5.3 Determination of Percentage Recovery

The recovery percentage was carried out by GC-FID; the analytes eluted from SPE tube were collected and then analyzed using a Hewlett Packard Model 6890GC gas chromatography (GC) equipped with a flame ionization detector (FID) and a data processor. The gas chromatographic column used was Ultra-1 932530, a non-polar, fused-silica capillary column (30 m length  $\times$  250  $\mu$ m inner diameter  $\times$  0.20  $\mu$ m film thickness). Helium gas was used as the carrier gas with a flow rate of 1.1 mL/min at a pressure of 75 kPa. The injector temperature was set at 250°C and the detector temperature was set at 310°C. The gas chromatography oven was operated under programmed temperature with an initial temperature of 100°C, which was held for 2 minutes and ramped up to 140°C with the rate of 5°C/min (Figure 3.4). Each sample (1  $\mu$ L) was injected into the gas chromatograph by using a 10  $\mu$ L syringe obtained from Agilent; USA. Triplicate injections were carried out for each sample to obtain a measure of accuracy.



**Figure 3.4** The Programmed Temperature

#### 3.5.4 Determination of Response Factor

The response factors,  $F$ , of internal standard (butyrophenone) and the test compounds (benzaldehyde, *p*-cresol, 2-chlorophenol, nitrobenzene) were determined by injecting 1  $\mu\text{L}$  of each stock solution (with the concentration of 100 000 ppm) into the gas chromatograph. Triplicate injections were carried out to obtain a more accurate and precise data. The equations used to calculate the response factor is shown below:

$$F = \frac{\text{Test compound / Internal standard peak area}}{\text{Test compound / Internal standard concentration}} \quad (3.1)$$

$$F = \frac{\text{Test compound / Internal standard peak area}}{100,000} \quad (3.2)$$

### 3.5.5 Determination of Concentration and Recovery Values of Test Compounds

The concentration of each test compound was calculated using the response factor obtained previously as shown below.

$$\text{Concentration, } M_x = \frac{F_s}{F_x} \times \frac{A_x}{A_s} \times \text{Concentration, } M_s \quad (3.3)$$

$M_x$  = Test compound concentration (ppm)

$M_s$  = Internal standard concentration (ppm)

$F_s$  = Internal standard response factor

$F_x$  = Test compound response factor

$A_s$  = Internal standard peak area

$A_x$  = Test compound peak area

The equations for calculating the recovery values are as follows:

$$\% \text{ Recovery} = \frac{M_x}{\text{Sample's concentration before extraction}} \times 100\% \times \text{Dilution Factor} \quad (3.4)$$

$$\% \text{ Recovery} = \frac{M_x}{100,000} \times 100\% \times 50 \quad (3.5)$$

$$\text{Dilution Factor} = \frac{\text{Test compound's volume after extraction}}{\text{Test compound's volume before extraction}} \quad (3.6)$$

$$\text{Dilution Factor} = \frac{5.0 \text{ mL}}{0.1 \text{ mL}} = 50 \quad (3.7)$$

Dilution factor for internal standard is:

$$\text{Dilution Factor} = \frac{5.0 \text{ mL}}{0.05 \text{ mL}} = 100 \quad (3.8)$$

### 3.5.6 Hypothesis Test

Hypothesis test was carried out to prove whether there is a significant difference among the data obtained. Here,  $t$ -test was carried out as the hypothesis test where the population variance,  $\sigma_1^2$  and  $\sigma_2^2$  was unknown and assumed difference,  $\sigma_1^2 \neq \sigma_2^2$  and the size of sample,  $n_1$  and  $n_2$  is small ( $n_1 < 30$ ,  $n_2 < 30$ ).

Null hypothesis,  $H_0 = \mu_1 - \mu_2 = \mu_0 = 0$

Alternative hypothesis,  $H_1 = \mu_1 - \mu_2 > 0$

Level of significance,  $\alpha = 0.05$

$$t_{\text{test}} = \frac{X_1 - X_2 - \mu_0}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}} \quad (3.9)$$

$$\text{Degree of freedom, } v = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{\left(\frac{s_1^2}{n_1}\right)^2}{n_1 - 1} + \frac{\left(\frac{s_2^2}{n_2}\right)^2}{n_2 - 1}} \quad (3.10)$$

$\mu_1 - \mu_2$  = Difference between two population's mean

$X_1$  = Mean for Sample 1

$X_2$  = Mean for Sample 2

$s_1$  = Standard deviation for Sample 1

$s_2$  = Standard deviation for Sample 2

$n_1$  = Numbers of data in Sample 1

$n_2$  = Numbers of data in Sample 2

$v$  = Degree of freedom

If  $t_{\text{test}} > t_{\alpha, v}$ ,  $H_0$  is rejected, which means that there is significance difference between the two values and if  $t_{\text{test}} < t_{\alpha, v}$ ,  $H_0$  will be accepted which means that there is no significance difference between the two values.

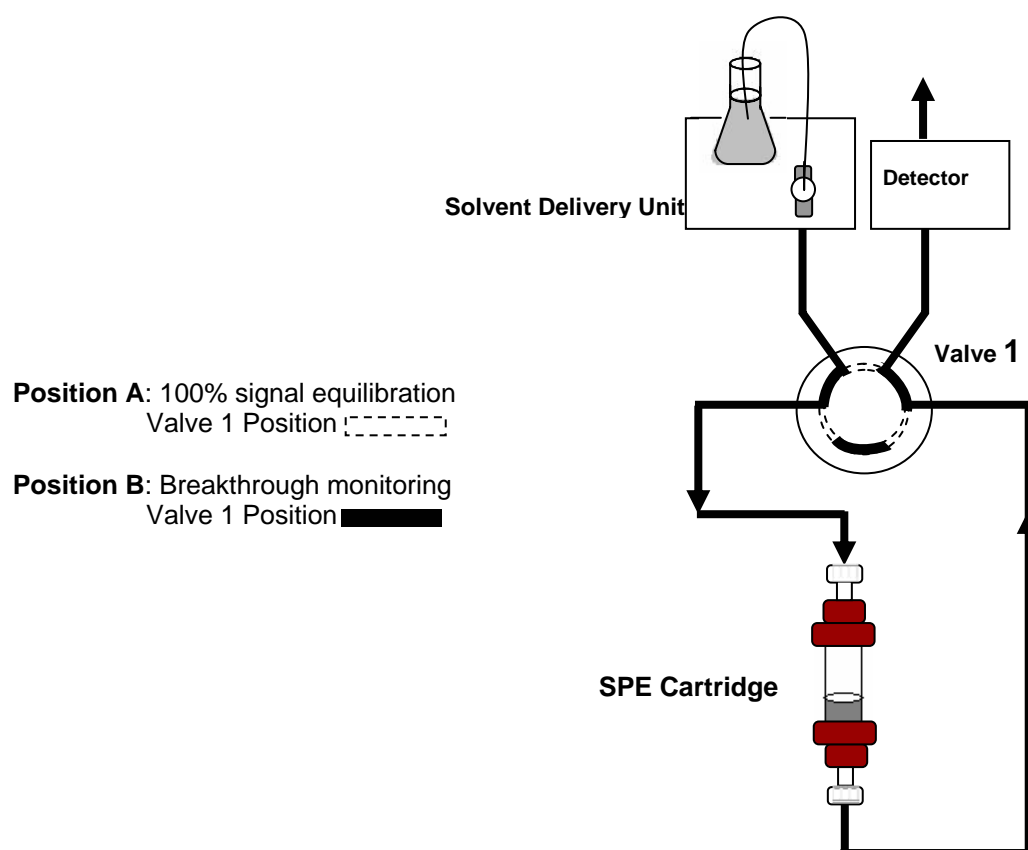
### 3.5.7 Determination of Breakthrough Volume

Breakthrough volume curves were acquired with a JASCO Waters-515 HPLC (Japan) Pump and a JUSCO Intelligent UV 2075 plus UV/Vis detector (Japan). All measurements were performed at 254 nm for nitrobenzene solution, and 280 nm for 2-chlorophenol solutions. Data acquisitions were made using a Hewlett-Packard NP3396A integrator.

Frontal analysis was used to measure the breakthrough of the solid phase extraction tubes [10]. Frontal analysis performed by pumping a dilute solution of the analyte (20 ppm 2-chlorophenol, and 20 ppm nitrobenzene) through the bed and examining the resulting detector response as a function of a time. The principles of operation of the frontal analysis are as follows: A solution is pumped through the cartridge bypass and directly to detector, as shown in Figure 3.5, position A. This provides a high detector signal, showing the absorbance corresponding to 100% breakthrough. The valve is then switched, causing the analyte solution to pass through the SPE (Fig.3.5, position B), resulting in 0% detector signal because the analyte is retained on the SPE cartridge. Eventually, after the cartridge becomes saturated with the analyte and it starts to breakthrough. This delay is called the breakthrough volume, which is a measure of the sorbent capacity. The following is formula equation of the breakthrough volume:

$$\text{Retention time} = \frac{\text{Retention distance}}{\text{Chart speed}} \quad (3.11)$$

$$\text{Breakthrough volume} = \text{Retention time} \times \text{Flow rate} \quad (3.12)$$



**Figure 3.5** Plumbing Configurations for Measurement of Breakthrough Volume of Sorbents for SPE

## **CHAPTER 4**

### **PREPARATION AND PHYSICAL CHARACTERIZATION OF PS-DVB AND MODIFIED PS-DVB ADSORBENTS**

#### **4.1 Introduction**

In the past few decades, a functional polymer network has gained great importance in many fields of scientific research as well as for industrial applications. In this research, a series of porous poly (styrene-divinylbenzene) (PS-DVB) copolymers were prepared by aqueous suspension polymerization in the presence of diluents that act as precipitants. Three different methods were utilized to modify the PS-DVB copolymer: (i) Friedel-Crafts acylation reaction by using stearoyl chloride as acylation agent, (ii) chloromethylation by using chloromethyl styrene and (iii) A novel modification method based on Williamson ether reaction that formed ether linkage on to PS-DVB. The chemically modified PS-DVB adsorbents were further examined using physical characterization methods.

This chapter presents and discussion the experimental data obtained in the preparation and physical characterization of the adsorbents. The latter includes characterization and interpretation by infrared analysis, nitrogen adsorption analysis, scanning electron microscopy, and thermogravimetric analysis of the modified PS-DVB as well as the unmodified PS-DVB adsorbents. Chemical characterization of the adsorbents was also performed on the adsorbents through solid phase extraction (SPE) analysis and these are discussed in Chapter 5.



## 4.2 Preparation of PS-DVB

Porous PS-DVB beads were prepared by using suspension copolymerization method. The copolymerization reaction was carried out using vinyl monomers and divinylbenzene as the cross-linking agent in presence of inert diluents. The reactor temperature was maintained at 70°C throughout the experiment in order to obtain droplets with good shape. Benzoyl peroxide (BPO) was used in the reaction and worked as an initiator. The final product was white powdery PS-DVB copolymer (Figure 4.1).



**Figure 4.1** Home-made PS-DVB Copolymer

The polymerization reaction is a batch process. Both styrene and divinylbenzene, which were in liquid form, were added into the reactor with an equivalent amount of water. The reaction was carried out by agitation of styrene and divinylbenzene with water and the mixture was dispersed into small globules. The chemical reactor was equipped with an agitator (see Figure 3.1), which mixed the water/organic chemical solution. BPO was added to initiate polymerization of the monomer's double bonds.

In order to control the particle size and prevent globules from agglomerating into a big unmanageable mass, small amounts of poly (vinyl alcohol) were added as suspension stabilizers. The poly (vinyl alcohol) can form a protective layer on the surface of the globules, which avoid the agglomeration upon collision. When the speed of agitation increased, the styrene/DVB existed in large globules material will break up into smaller droplets until reaching the size of about one micrometer. In this process, the polymerization reaction initiated by the addition of BPO will caused the styrene/DVB molecules to transform into small plastic beads.

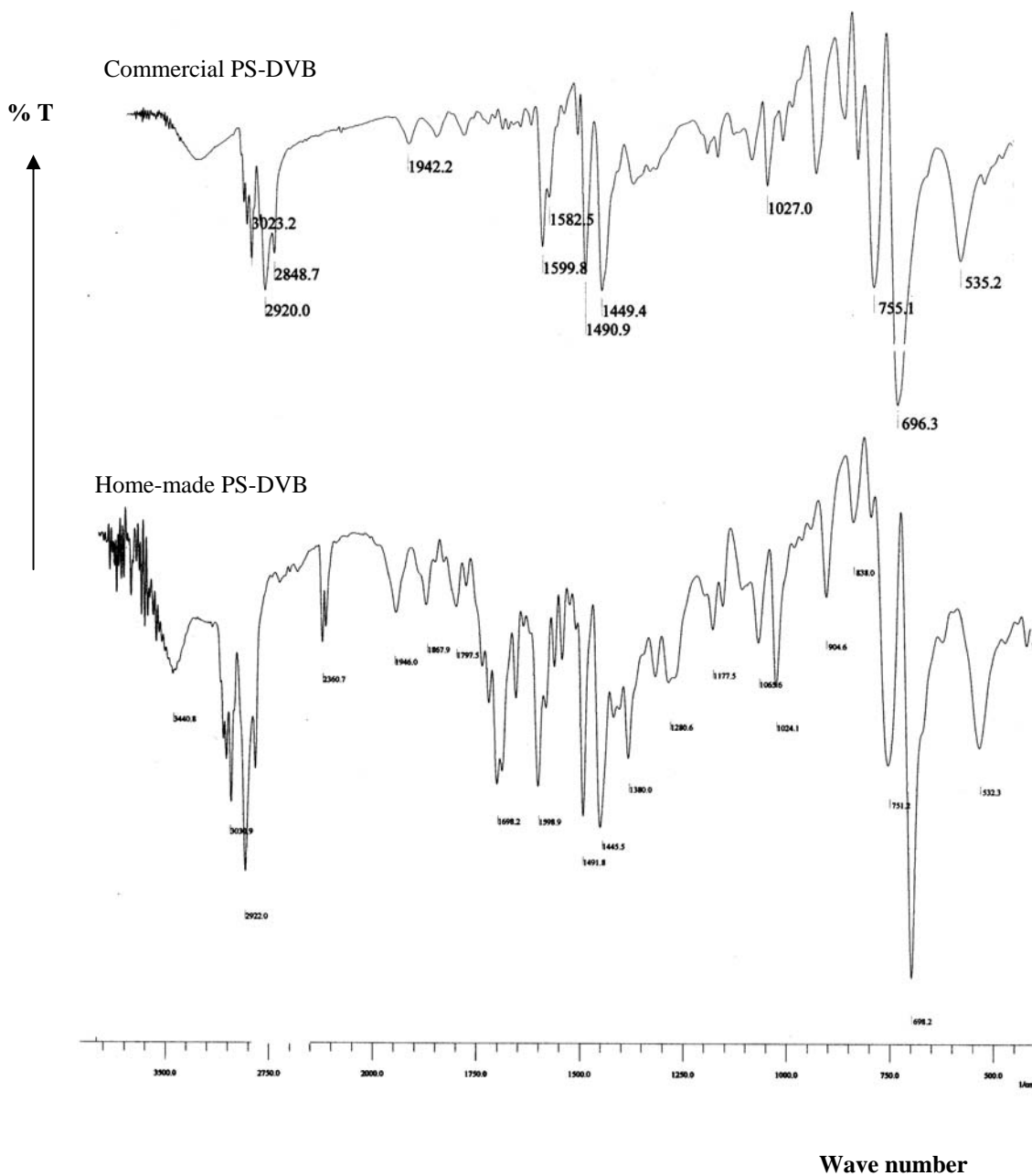
### **4.3 Physical Characterization for Unmodified PS-DVB**

Characterizations were carried out on home-made PS-DVB and subsequently compared with the commercial PS-DVB in order to verify whether the home-made PS-DVB was successfully synthesized. The physical characterizations included:

- a. Fourier transform infrared spectroscopy (FTIR)
- b. Scanning electron microscopy (SEM)
- c. Nitrogen adsorption analysis
- d. Thermogravimetric analysis

#### **4.3.1 FTIR Spectroscopic Characterization**

In the physical characterization by FTIR spectroscopic method, the FTIR spectra obtained from the synthesized and commercial PS-DVB adsorbents can be evaluated and subsequently compared. Figure 4.2 shows the FT-IR spectra for the commercial and home-made PS-DVB adsorbents, respectively. The finger print region between  $1400\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$  was very important in identifying the compounds. Calibrated wave numbers were believed to be accurate within records by using KBr pellets with a concentration of 1:100 and scan time of 10 min at room temperature. The position and characteristic of bands observed (Table 4.1) were in good agreement with those reported in the literatures [41].



**Figure 4.2** FTIR Spectra of (a) Commercial PS-DVB and (b) Home-made PS-DVB

The IR spectrum of home-made PS-DVB (b) exhibited an absorption band at  $3034.9\text{ cm}^{-1}$  attributed to C-H ( $\text{sp}^2$ ) of aromatic asymmetric. In addition, bands at  $1589.9\text{ cm}^{-1}$ ,  $1491.8\text{ cm}^{-1}$ , and  $1445.5\text{ cm}^{-1}$  supported the presence of C=C phenyl stretching. The bands at  $751.2\text{ cm}^{-1}$  and  $696.2\text{ cm}^{-1}$  were attributed to presence of out-of-plane bending of monosubstituted benzenes.

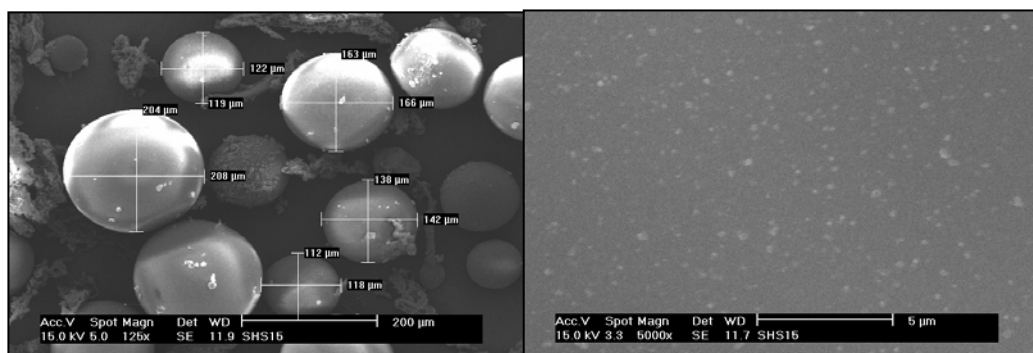
**Table 4.1:** Infrared Frequency ( $\text{cm}^{-1}$ ) for Home-made and Commercial PSDVB

Characteristic Vibration	Wave number, $\text{cm}^{-1}$	
	Home-made PS-DVB	Commercial PSDVB
Aromatic CH	3034.9 sharp	3023.2 sharp
C=C phenyl	1589.9, 1491.8, and 1445.5	1599.8, and 1449.4
-CH saturated	2922.0	2921.0 and 2848.7
Monosubstituted benzene	751.2 and 696.2	755.1 and 696.3

It can be seen that the FTIR spectrum for home-made PS-DVB (b) is similar to the FTIR spectrum of the commercial PS-DVB (a). This indicates that the home-made PS-DVB had the same structural properties as the commercial PS-DVB, hence, suggesting that PS-DVB was successfully synthesized in the laboratory.

#### 4.3.2 Characterizations of Particle Size, Surface Morphology and Pore Width / Volume by Scanning Electron Microscopy and Nitrogen Adsorption Analysis




Scanning electron microscopy (SEM) was carried out to identify the particle size and surface morphology for the PS-DVB beads. Figure 4.3 shows the surface morphology of the home-made PS-DVB. It was observed that the PS-DVB shows a heterogeneous surface morphology and its average particle size was approximately 115  $\mu\text{m}$ . Hence, the PS-DVB fulfilled the major criteria needed for support material.

a). Magnification was at 125  $\times$ b). Magnification was at 5000  $\times$ **Figure 4.3** Surface Morphology of Home-made PS-DVB

A set of experiments was carried out to determine the effect of stirrer design on the average particle size and pore width. It was intended to investigate which stirrer design could produce PS-DVB beads with suitable particle size. There were three types of stirrer designs investigated, namely single cross-blade impeller, half moon impeller, and double cross-blade impeller.

Table 4.2 shows the effect of stirrer design to the PS-DVB particle size and porosity. By using single cross-blade impeller stirrer, an average particle size of 74  $\mu\text{m}$  was obtained. The particle size was slightly smaller relative to those obtained using other stirrer designs. When the polymerization was carried out using half-moon impeller stirrer, an average particle size of approximately 116  $\mu\text{m}$  was obtained. The half moon impeller, which only had two blades, did not have agitation problem unlike the single blade impeller stirrer. Double cross blade impeller that has eight blades generally resulted in strong agitation problem. This might be due to the position of the stirrer in the reactor. The double cross blade impeller was not placed in the center of the reactor and this lead to inconsistent shaking in the reactor.

**Table 4.2:** Effect of Stirrer Design to PS-DVB Particle Size and Porosity

Type of Stirrer	Average particle size ( $\mu\text{m}$ )	Average pore width ( $\text{\AA}$ )	Total pore volume ( $\text{cm}^3/\text{g}$ )
 Cross blade impeller	74 $\mu\text{m}$	38	0.000523
 Half-moon impeller	116 $\mu\text{m}$	184	0.003151
 Double cross blade impeller	120 $\mu\text{m}$	76	0.001840

Among the various factors that influence the particle size of the product, stirring speed is the most important factor that provides a relatively convenient means of particle size control for most practical purposes. The particle size can be controlled by the adjustment of the stirring speed. These limits depend on the size and the configuration of the polymerization reactor (including its stirring arrangement). For the laboratory preparation involving a total volume of about 500 mL, the stirring speed can be varied in the range of 200 to 1000 rpm. The stirring speed of 900 rpm was chosen in our study.

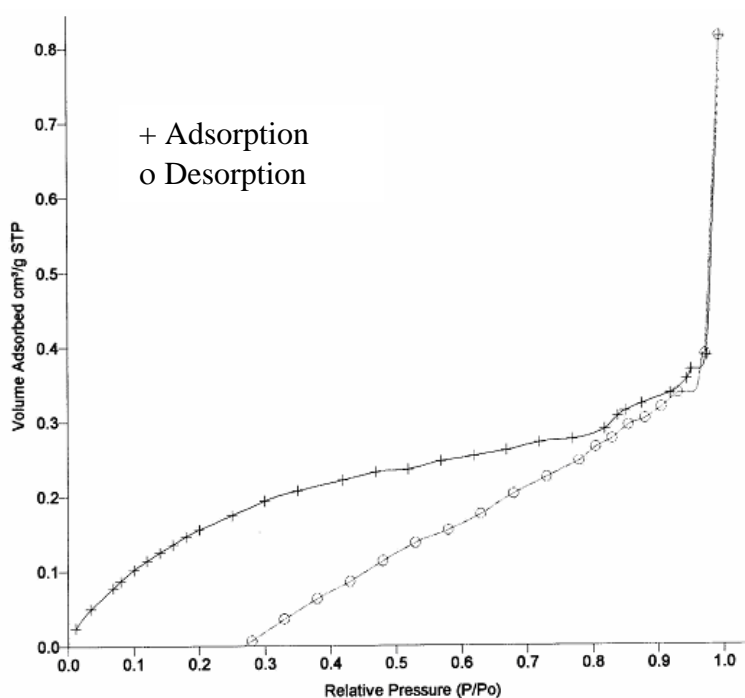
The home-made PS-DVB was further characterized by using nitrogen adsorption analysis. The nitrogen adsorption analysis was carried out to identify the types of pore of the home-made PS-DVB. Pore width and pore volume are the results usually obtained from this analysis. Pore width is an important parameter that describes the pore structure of a porous copolymer. The pore volume and the average pore width of copolymer particles usually depend on the reaction time and stirrer design. The reaction times used in our study were 1 h, 5 h, 10 h, 15 h, and 20 h. The reaction time optimization was aimed to find out the optimal reaction time required to produce PS-DVB adsorbents with high average pore width with acceptable pore volume. A good adsorbent usually give wide average pore width and pore volume. This can lead to high adsorption capacity for the adsorbent.

Table 4.3 shows physical characteristics of the home-made PS-DVB compared to commercial PS-DVB. In can be observed that the average pore width for the home-made PS-DVB was 184 Å, which can be classified as mesopores. Mesopores usually exist with the pore width in the range of 20 Å-500 Å. The pores are irregular, voids between clusters of globules (mesopores) or voids inside a globule (micropores). The hydrodynamic volume of the dissolved molecules controls access to the pores. Molecules will only enter into those pores that are able to accommodate their size while smaller pores remain inaccessible for stearic reasons [48].

**Table 4.3:** Physical Characteristics of the Home-made PS-DVB Compared to Commercial PS-DVB

Sample	Average pore width (Å)	Total pore volume( $\text{cm}^3/\text{g}$ )
Home-made PS-DVB	184	0.003151
Commercial PS-DVB	60	0.001009

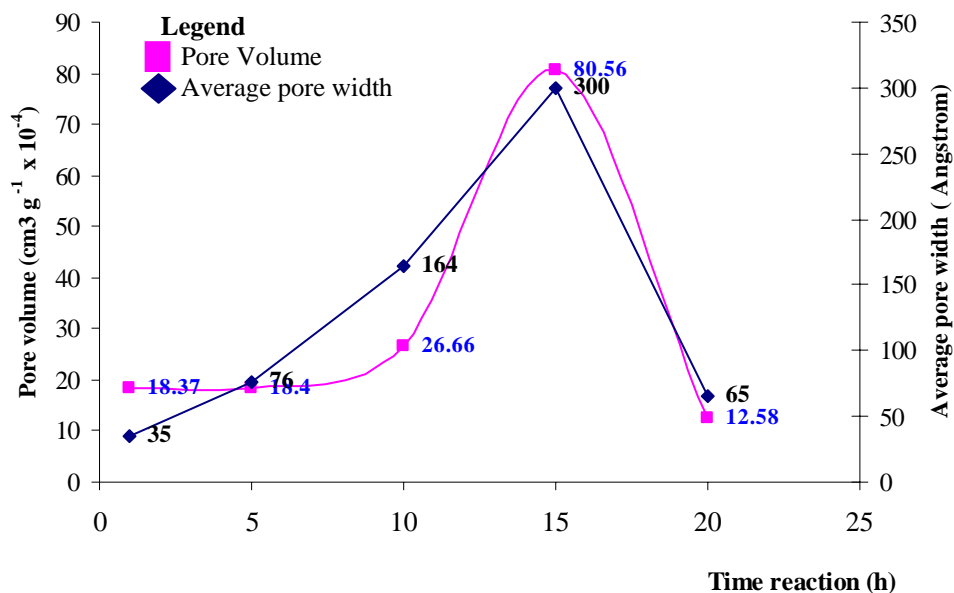
The home-made PS-DVB was found to have low BET surface area, similar to commercial PS-DVB. Due to the small BET surface area ( $<10 \text{ m}^2/\text{g}$ ), the instrument was unable to analyze the sample accurately. From the result obtained (Figure 4.4), it can be seen that the isotherm adsorption for home-made PS-DVB was generally not well formed.



**Figure 4.4** Nitrogen Adsorption Isotherm Plot of Home-made PS-DVB

Figure 4.5 shows the effect of reaction time to the porosity and particle size of PS-DVB. It can be observed that when reaction time was set at 1 h, the pore width of PS-DVB was approximately 35 Å. Highest average pore width value and pore volume were obtained when the reaction time was fixed at 15 h with a value of

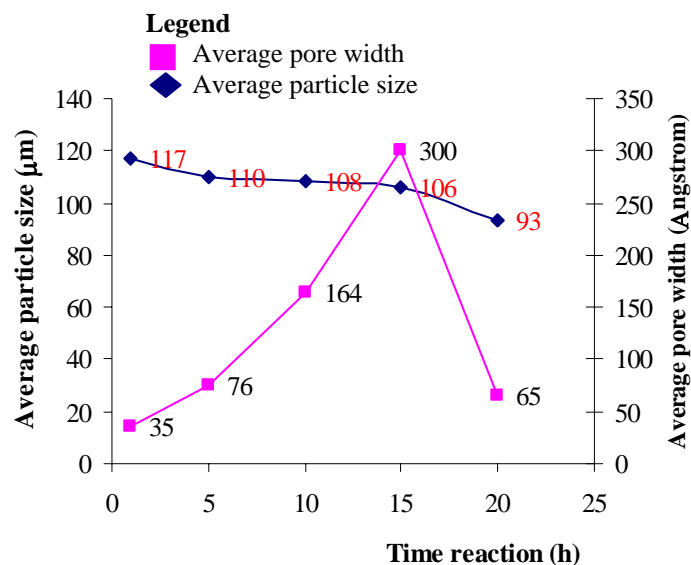
300 Å. However, a significant decrease of pore width was noted when the reaction time was increased to 20 h, due to 65 Å compare to others. The average pore width was somewhat in linear ratio with pore volume. This represent that the pore width was directly proportional to the pore volume.



**Figure 4.5** The Effect of Reaction Time on Pore Volume and Average Pore Width of Home-made PS-DVB

The particle size was generally affected by the total reaction time. Figure 4.6 shows the effect of reaction time on the average particle size and average pore width for PS-DVB. It can be seen that when the reaction time was 1 h, the particle size for PS-DVB was 117 µm. The highest average pore width value and pore volume were obtained when the reaction time was increased to 15 h. However, when the reaction time was further increased to 20 h, the particle size became smaller and fine with particle size was decreased to 93 µm. Hence, reaction time at 15 h was chosen as the optimum reaction time for our study.



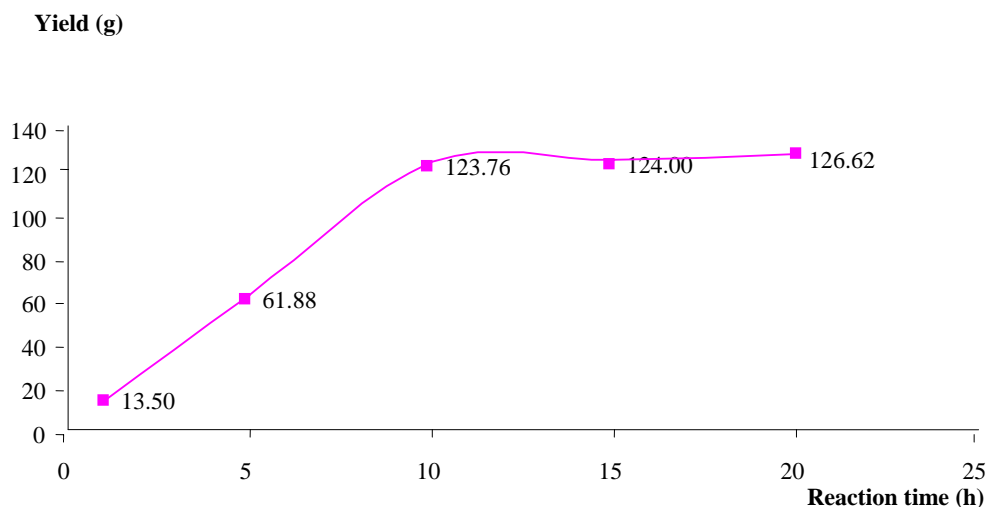


**Figure 4.6** The Effect of Reaction Time to the Average Particle Size and Average Pore Width of Home-made PS-DVB

The reaction time also affected the amount of PS-DVB obtained after reaction was completed. In our research, it was found that longer reaction times tend to increase the total amount of PS-DVB obtained. Figure 4.7 shows the effect of the reaction time to the yield of home-made PS-DVB. It can be seen that when the reaction time was 1 h, the yield was only 13.50 g. This was probably due to the reaction time that was not long enough for complete copolymerization reaction. When the reaction time was increased to 5 h, the yield increased dramatically to 61.88 g. However, when the reaction time was further increased to 20 h, a maximum yield of 126.62 g was obtained. Hence, it can be concluded that the yield increases with increased reaction time until it reaches a maximum value after complete reaction.

In general, the total amount of PS-DVB yield was low for short reaction time (<5 h) but the yield increased for longer reaction time (10-20 h). It was noted that when polymerization was stopped at 1-5 h, the product obtained contain strong odor of styrene. On the other hand, there was no styrene odor of the final products obtained with reaction time of 10 h or longer where the yield began to level off and reached a high value of 126.62 g for the reaction time of 20 h. Based on the mass balance theory, the yield of product was 129.60 g. It means that the yield of product

obtained by experimental was similar with the yield of product by mass balance theory.



**Figure 4.7** Effect of Reaction Time to the Yield of Home-made PS-DVB

#### 4.3.3 Thermal Stability by Thermogravimetric Analysis

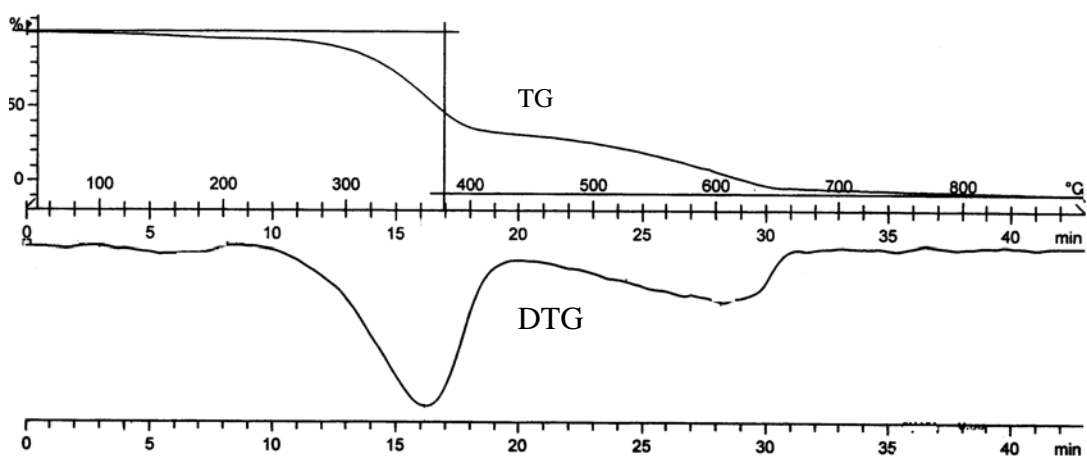
In this research, a series of thermogravimetric analyses (TGA) were carried out to examine the thermal stability of the PS-DVB adsorbents. In addition, the limits of the operating temperature for the adsorbents can also be identified to increase the adsorbent lifetime. Thermogravimetric analysis of home-made PS-DVB adsorbent was compared with commercial PS-DVB.

Based on the TGA thermograms illustrated (Figure 4.8), the thermograms for home-made PS-DVB and commercial PS-DVB were almost identical. It was observed that a sharp inflection occurred in the temperature range of 300-500°C. When the temperature was increased from 230°C to 520°C, the PS-DVB started to decompose until the decomposition was almost come to completion. A significant reduction of the rate of weight loss was noted after the temperature was further increased to 710°C.

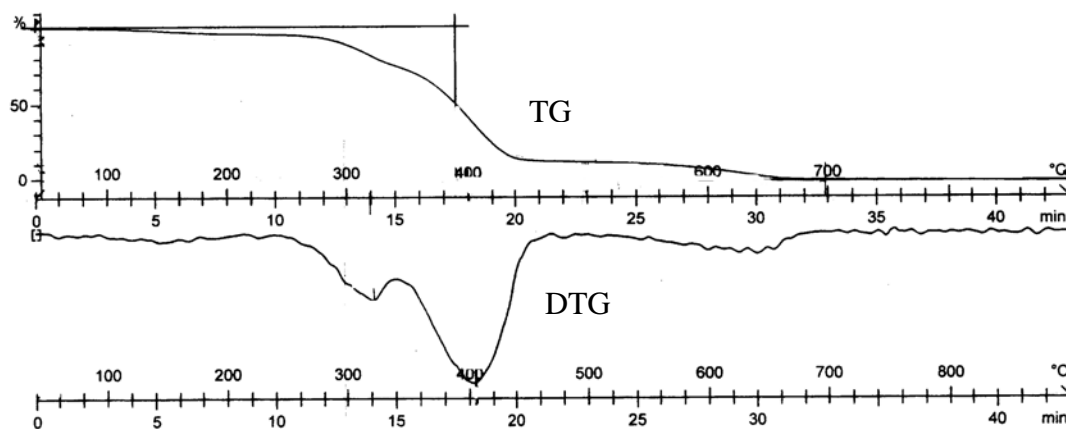
Typical derivative thermogravimetric (DTG) thermogram for PS-DVB is presented in Figure 4.8. The thermograms of home-made PS-DVB clearly indicates the occurrence of a very sharp peak at 400°C, followed by two smaller peaks at

320°C and 620°C respectively. The sharp peak observed at low temperatures range was probably due to the removal of water and C=C phenyl molecules from the sample. The smaller peaks that occurred at temperature range of 260°C to 340°C might be due to the evolution of physically entrapped more stable organic compounds in the sample. Another sharp peak noted at 420°C probably corresponded to the removal of C=C molecules derived from phenyl groups.

The DTG thermograms (Figure 4.8) observed for home-made PS-DVB and commercial PS-DVB were almost identical. Both of them had two functional group peaks that differ in thermal stability. The peaks for home-made PS-DVB were observed at 320°C and 420°C. As for the commercial PS-DVB, the peak was located at 360°C, and 600 °C. When the temperatures were further increased to 710°C; both of home-made PS-DVB and of commercial PS-DVB lose their weight completely. This phenomenon was due to the decomposition of the chemical bonding of PS-DVB at these temperatures.



(a). TG and DTG thermogram for commercial PS-DVB



(b). TG and DTG for home-made PS-DVB

**Figure 4.8** Thermogravimetric (TG) and Derivative Thermogravimetric (DTG), thermograms of (a). Commercial PS-DVB and (b).Home-made PS-DVB

Table 4.4 shows the thermal degradation results obtained from thermogravimetric analysis of the home-made PS-DVB and commercial PS-DVB adsorbents. The thermal degradation of PS-DVB occurred in three stages. The commercial PS-DVB started to decompose at temperature range from 40°C to 230°C and the percentage weight loss of PS-DVB was 4.63%. This result was similar to the home-made PS-DVB with weight loss percentage of 4.54%. When reaching the stage II, both the home-made PS-DVB and commercial PS-DVB adsorbents were almost completely decomposed. The percentage weight loss for home-made PS-DVB and commercial PS-DVB were 85.33% and 72.68%, respectively. The total percentage weight lost calculated for both adsorbents examined were approximately 100% suggesting that both of the adsorbent were completely decomposed at temperatures around in the 800 °C.

**Table 4.4:** Physical Characteristics for Homemade PS-DVB and Commercial PS-DVB Obtained from Thermogravimetric Analysis

Sample	Weight loss (wt%) and temperature range ( °C ) for three stages of degradation		
	Stage I 40-230 °C	Stage II 230-520 °C	Stage III 520-900 °C
Home-made PS-DVB	4.54%	85.33%	10.13%
Commercial PS-DVB	4.63%	72.68%	22.69%

#### 4.4 Physical Characterization of Modified PS-DVB

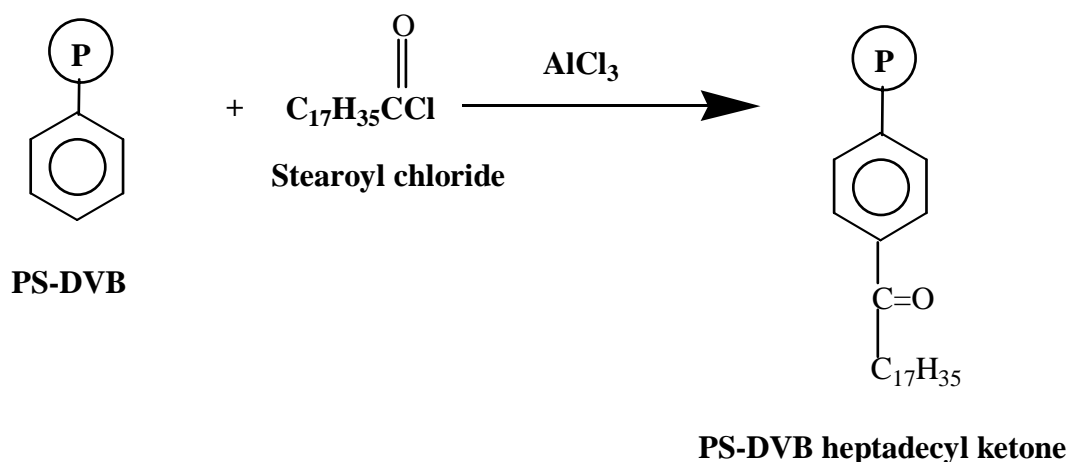
The PS-DVB adsorbents such as PS-DVB heptadecyl ketone, chloromethyl PS-DVB, and octadecoxy methyl PS-DVB have often been used in SPE extraction process, replacing other conventional adsorbents. PS-DVB adsorbents can either be unmodified PS-DVB or modified PS-DVB.

##### 4.4.1 Preparation of Modified PS-DVB and Characterization by FTIR

###### 4.4.1.1 Introducing Heptadecyl Ketone ( $C_{17}H_{35}CO-$ ) onto PS-DVB

The cross-linked polymer was functionalized via Friedel-Crafts acylation reaction by using stearoyl chloride in the presence of anhydrous  $AlCl_3$  as the Lewis acid catalyst and 1,2-dichloroethane as the solvent. The reactions were operated at room temperature in order to avoid the resin from over swelling and crushing correspondingly. The reaction occurred rapidly and required overnight reaction.

Formation of PS-DVB heptadecyl ketone adsorbent is illustrated in Figure 4.9. Friedel-Crafts reactions will not occur with aromatic rings that have strong deactivating substituents such as nitro, carbonyl, and sulfonyl groups.



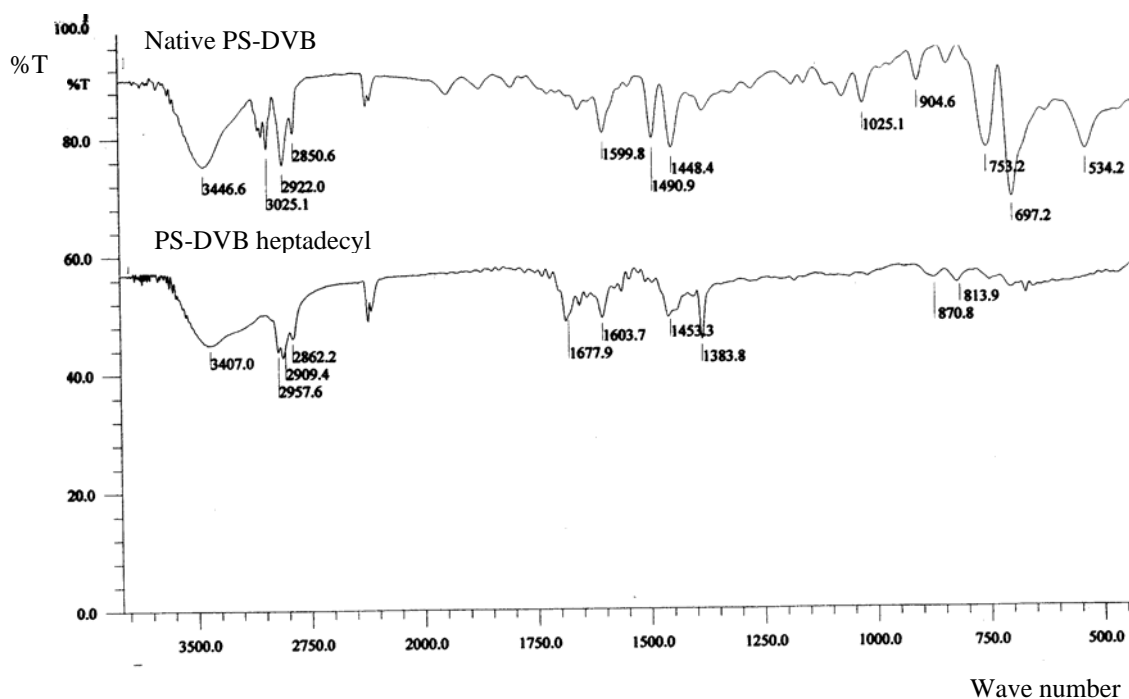
**Figure 4.9** Formation of PS-DVB Heptadecyl Ketone. “P” Represents Bulk PS-DVB Polymer

The modification reaction was carried out as described in section 3.2.2. The colour of the modified PS-DVB beads was yellowish brown after drying at 80°C for 12 hours. The color of the modified PS-DVB was due to the bonding of a carbonyl group to the phenyl ring of polystyrene that varies the absorption band of the newly formed product.

FTIR spectra of native PS-DVB and PS-DVB-heptadecyl ketone adsorbents are illustrated in Figure 4.10. The band at 1677.9 cm<sup>-1</sup> was related to asymmetrical C=O stretching that indicated the incorporation of these functional groups to the PS-DVB. The absorption band at 2957.6 cm<sup>-1</sup> was related to =C-H aromatics stretching. Bands at 2909.4 cm<sup>-1</sup> and 2862.2 cm<sup>-1</sup> were related to the stretching of C-H alkenes respectively. The presence of benzene ring in this polymer was confirmed by the existence of absorption bands at 1603.7 cm<sup>-1</sup> and 1453.3 cm<sup>-1</sup> corresponding to the C=C aromatic stretching. The absorption band corresponding to the carbonyl group was shifted to the right and lower frequency because of the conjugation effect between the carbonyl group with the benzene ring. Meanwhile, the similarities

between the spectra of the native PS-DVB and PS-DVB heptadecyl ketone adsorbents indicated that the basic structural units were preserved in the polymer.

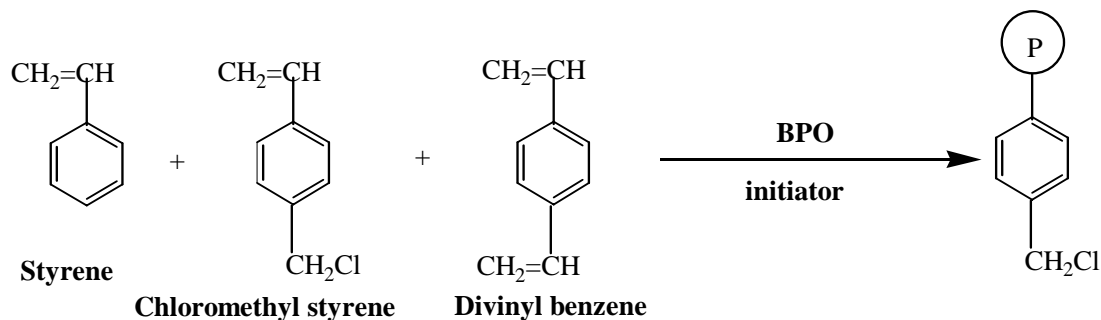
The FTIR spectrum of the home-made PS-DVB did not show peaks at  $1683.7\text{ cm}^{-1}$ , and  $1603.7\text{ cm}^{-1}$ , which means that the modified stearoyl chloride-modified PS-DVB was successfully obtained.



**Figure 4.10** Infrared Spectra of Native PS-DVB and PS-DVB-Heptadecyl Ketone

#### 4.4.1.2 Introducing Chloromethyl Group ( $-\text{CH}_2\text{Cl}$ ) onto PS-DVB

This reaction involves the replacement of a hydrogen atom on the aromatic ring by a  $\text{CH}_2\text{Cl}$  group in single operation. This reaction occurs through the interactions between chloromethyl-styrene, styrene, and divinyl benzene, in the presence of initiator such as benzoyl peroxide [37, 38]. The overall reaction mechanism is shown in Figure 4.11.



**Figure 4.11** Preparation of Chloromethyl PS-DVB. BPO = Benzoyl Peroxide, “P” Represents Bulk PS-DVB Polymer

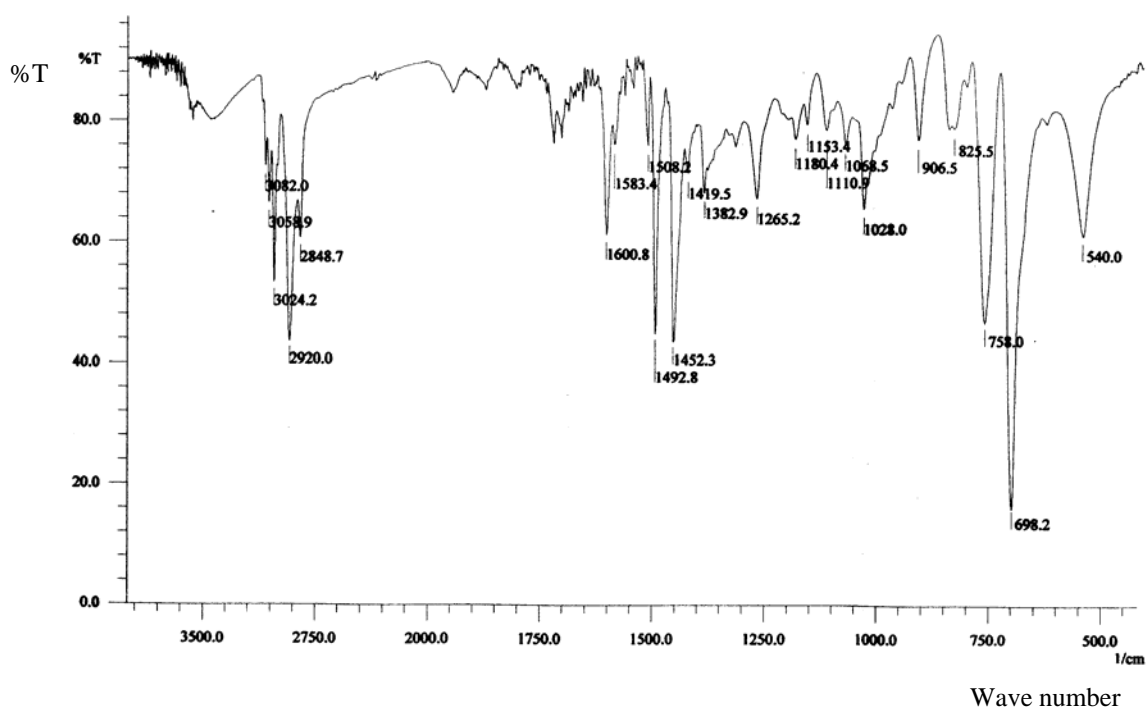
Bacquet, and Caze [37] have reported the decrease of vinyl group is due to the addition of the chloromethylating agent to the double bond. The aliphatic chlorine groups were identified by infrared spectroscopy (band at 698.2/cm) represented the benzyl chloride group in the PS-DVB spectrum.

The most versatile reaction on PS-DVB resins is probably chloromethylation. It is because the chloromethylated resins could be easily modified due to the high reactivity of the chloromethyl groups. Varieties of chloromethylating agents were required to chloromethylate the polymer in the presence of benzoyl peroxide.

Variations of reaction conditions such as excess usage of chloromethylating agents, higher temperature, different halogenated solvents, and reaction time have been proven to lead to incomplete reaction. Isolated polymer was found unchanged when the reaction temperature was maintained below 0°C, suggesting that the chloromethylation took place only at temperature higher than (>0°C). In all cases, the chloromethylation undoubtedly occurred under the reaction conditions, but the cross-linking took place rapidly as the active aromatic ring attacks the chloromethyl group in a Friedel-Crafts alkylation reaction. The chloromethylation depended dominantly on the reaction temperature and the substituents [36, 38].



Figure 4.12 shows an infrared spectrum of chloromethyl PS-DVB. It can be noted that the C=C stretching of the phenyl were located at  $1600.8 - 1583.4 \text{ cm}^{-1}$ , and  $1508.2 - 1492.8 \text{ cm}^{-1}$ . As for the monosubstituted benzene, the five adjacent hydrogen atoms resulted in two absorption bands close to  $758.0 \text{ cm}^{-1}$  and  $698.2 \text{ cm}^{-1}$ . The *para*-substituted compounds was represented by doublet centered at  $825.5 \text{ cm}^{-1}$ . The bands at  $758.0 \text{ cm}^{-1}$  and  $698.2 \text{ cm}^{-1}$  are attributed to the presence of C-Cl stretching that overlapped with the monosubstituted benzene. The peaks at  $2920.0 \text{ cm}^{-1}$ (s) and  $2848.7 \text{ cm}^{-1}$ (s), represent the aliphatic C-H stretching.



**Figure 4.12** The Infrared Spectrum of Chloromethyl PS-DVB

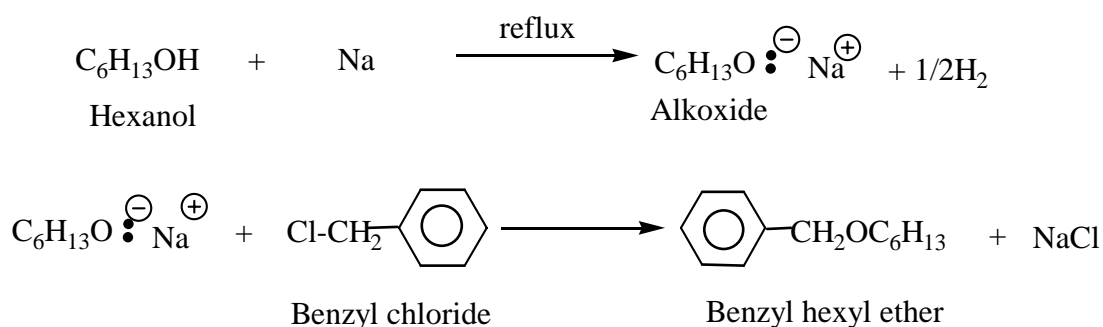
Table 4.5 summarizes dominant infrared frequencies for chloromethyl PS-DVB. The wide varieties of fingerprints are useful in structure functional group identification. The preparation of sample for infrared analysis by using KBr pellet can assist in eliminating the problem of bands due to the mulling agent. Hence, this techniques gave overall better spectrum except for band at  $3450 \text{ cm}^{-1}$  which represented the OH group caused by trace of water.

**Table 4.5:** Infrared Frequency for the Chloromethyl PSDVB

Characteristic Vibration	Wave number, $\text{cm}^{-1}$
=CH aromatic	3024.2 – 3082.0 (s)
C=C aromatic	1600.8 – 1452.3 (s)
-CH saturated	2920.0 (s), and 2848.7 (s)
Monosubstituted benzene	825.5 - 698.2 (s)
C-Cl stretching	758.0 and 698.2 (s)

#### 4.4.1.3 Williamson Ether Reaction

A reaction model based on preparation of benzyl hexyl ether was carried out in order to ascertain the feasibility of PS-DVB modification by Williamson ether reaction. A suggested mechanism of the Williamson ether reaction is shown in Figure 4.13. The first step of the Williamson ether synthesis consists of the reaction between metal (sodium) with an alcohol (hexanol) to form an alkoxide ion and hydrogen gas. Sodium alkoxides are strong bases and nucleophiles. Alkoxides can react with benzyl chloride to produce ether (benzyl hexyl ether). This Williamson ether reaction involved  $\text{S}_{\text{N}}2$  displacement with backside attached by the alkoxide [6, 58].

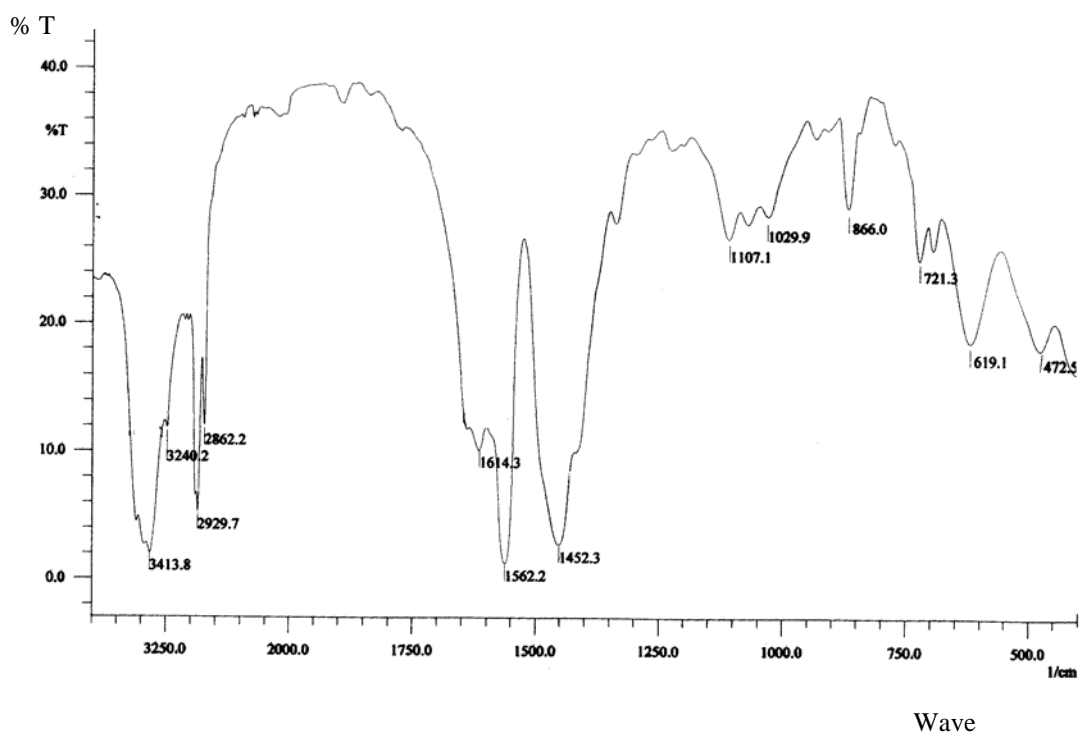


**Figure 4.13** Reaction for the Preparation of Benzyl Hexyl Ether as A Reaction Model [6]

#### 4.4.1.3(a) Preparation of Benzyl Hexyl Ether as Reaction Model

A significant characteristic of aromatic compounds in infrared spectra is the presence of relatively large number of sharp bands, especially close to the region of  $3030\text{ cm}^{-1}$  due to  $=\text{C-H}$  stretching vibrations. Other important bands are located in the region range of  $1600\text{--}1450\text{ cm}^{-1}$  which resulted from the in-plane skeletal vibrations of the aromatic ring.

From the spectrum illustrated in Figure 4.14, it can be seen that the bands for  $\text{C}=\text{C}$  stretching phenyl ring vibration are located at  $1614.3\text{ cm}^{-1}$ ,  $1562.2\text{ cm}^{-1}$ , and  $1452.3\text{ cm}^{-1}$ . The intensities of the other bands are the band near  $1562.2\text{ cm}^{-1}$  that is sharp and appear as shoulder on the side of  $1614.3\text{ cm}^{-1}$  band, and  $1452.3\text{ cm}^{-1}$ . The ethers display a weak  $\text{C-O}$  stretch absorption at  $1107.1\text{ cm}^{-1}$ , which varies only slightly from ether to absorption of primary ether.

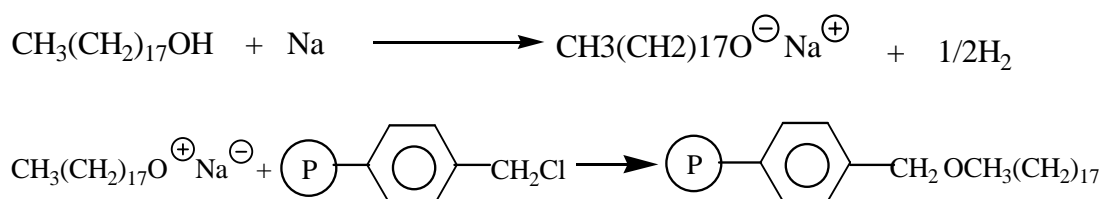


**Figure 4.14** Infrared Spectrum of Benzyl Hexyl Ether

Some general features illustrative of the philosophy relating to the interpretation of spectra and correlation of absorption bands in the presence of particular groups should be noted. It will be immediately apparent that this spectrum may be divided into two parts, the first between 4000-1600  $\text{cm}^{-1}$  and the second from 1600-660  $\text{cm}^{-1}$ . In plane bending of the unsaturated C-H bond gives rise to absorption in the 1420-1290  $\text{cm}^{-1}$  region which is frequently of weak intensity. This absorption occurs in the region of the spectrum associated with C-C stretching and saturated C-H bending. The  $\text{CH}_2$  asymmetric and symmetric vibrations which occur near 2929.7  $\text{cm}^{-1}$  and 2862.2  $\text{cm}^{-1}$ , respectively, are clearly visible. The absorption maximum for the carbon-hydrogen stretching frequency lies in the general region around 3000  $\text{cm}^{-1}$ ; for  $sp^2$ -hybridized carbon the position is just above 3000  $\text{cm}^{-1}$ , i.e. C-H aromatic.

#### 4.4.1.3(b) Introducing Octadecoxy ( $\text{C}_{18}\text{H}_{37}\text{-O-}$ ) onto Chloromethyl PS-DVB

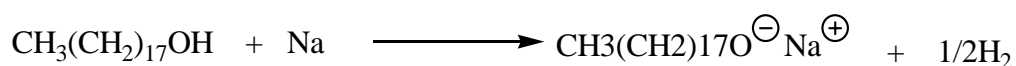
Preparation of octadecoxy methyl PS-DVB was based on the model reaction (see 4.4.1.3 (a)). In this study, grafting octadecoxy onto polymeric resin was successfully prepared. The alkoxide (octadecoxy) was prepared by the reaction of the corresponding alcohol with an active metal such as sodium. The resulting octadecoxy ( $\text{C}_{18}\text{H}_{37}\text{-O-}$ ) was then reacted with the chloromethyl PS-DVB to produce the octadecoxy methyl PS-DVB (see Figure 4.15).



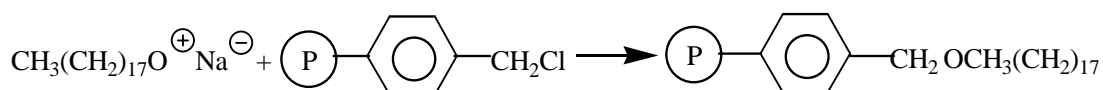
**Figure 4.15** The Reaction for the Preparation of Octadecoxy Methyl PS-DVB

The reaction routes of preparation of octadecoxy methyl PS-DVB are illustrated in Figure 4.16. Excess  $\text{CH}_3(\text{CH}_2)_{17}\text{ONa}$  was removed by dissolving and heating in toluene. Removal of  $\text{NaCl}$  from the yield was carried out by dissolving and heating in water.

Step I



Step II



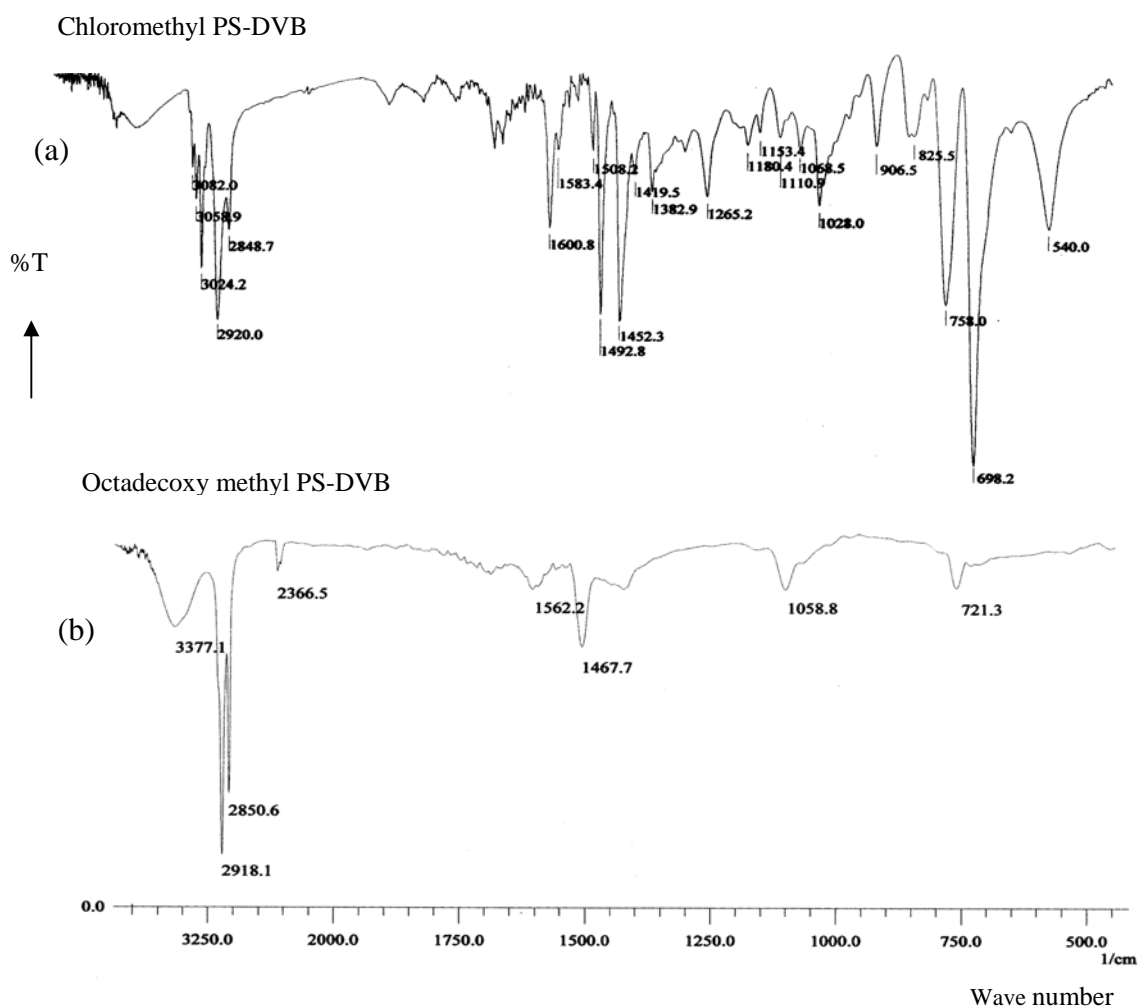
**Figure 4.16** The Reaction Routes of Preparation of Octadecoxy Methyl PS-DVB

The reaction involved an  $\text{S}_{\text{N}}2$  reaction where an alkoxide ion was replaced by halogen, sulfonyl, or sulfate group. In our research, alkyl halides were used. The alkoxide can be prepared by the reaction of the corresponding alcohol with an active metal such as metallic sodium or by using metal hydride such as  $\text{NaH}$  acting upon the alcohol. The resulting alkoxide salt was then reacted with the alkyl halide (sulfonate or sulfate) to produce ether in  $\text{S}_{\text{N}}2$  reaction [58]. Table 4.6 demonstrates the details of FT-IR data for modified octadecoxy methyl PSDVB and chloromethyl PS-DVB.

**Table 4.6:** The FT-IR Data of Modified Octadecoxy Methyl PSDVB Compare to Chloromethyl PS-DVB

Characteristic Vibration	Wave number, $\text{cm}^{-1}$	
	Chloromethyl PS-DVB (PSDVB- $\text{CH}_2\text{Cl}$ )	Octadecoxy methyl PS-DVB (PSDVB- $\text{CH}_2\text{-O-C}_{18}\text{H}_{37}$ )
=CH aromatic	3024.2, 3058.9, (s)	None
C=C stretching phenyl ring	1600.8 -1452,3 (s)	1562.2 (s), 1467.7 (s)
-CH <sub>2</sub> asymmetric and symmetric vibrations	2920.0, and 2848.7 (s)	2918.1, 2850.6 (s)
Monosubstituted benzene	758.0, and 698.2 (s)	721.3 (w)
C-Cl stretching	698.2 (s)	None
C-O-C (ether)	None	1058.8 (w)

Figure 4.17 shows the infrared spectra of chloromethyl PS-DVB compared with octadecoxy methyl PS-DVB. Figure 4.17(b) shows an IR spectrum of octadecoxy methyl PS-DVB. It exhibited bands for C-O at  $1058.8\text{ cm}^{-1}$  and while stretching bands at  $1562.2\text{ cm}^{-1}$  and  $1467.7\text{ cm}^{-1}$  were attributed for C=C of phenyl stretching. The presence of a band centered at  $2918.1\text{ cm}^{-1}$  was attributed to C-H strongly of the octyl chain. The absorption of CH<sub>2</sub> asymmetric bands for chloromethyl PS-DVB and octadecoxy methyl PS-DVB were noted at region around  $2918.1\text{ cm}^{-1}$  and  $2850.6\text{ cm}^{-1}$ , respectively. The bands at  $1562.2\text{ cm}^{-1}$  and  $1467.7\text{ cm}^{-1}$  were related to in-plane bond stretching for phenyl ring. Based on the spectra obtained, significant differences of intensity at  $698.2\text{ cm}^{-1}$  (due to C-Cl stretching) and  $1058\text{ cm}^{-1}$  (due to C-O-C stretching) regions were observed.

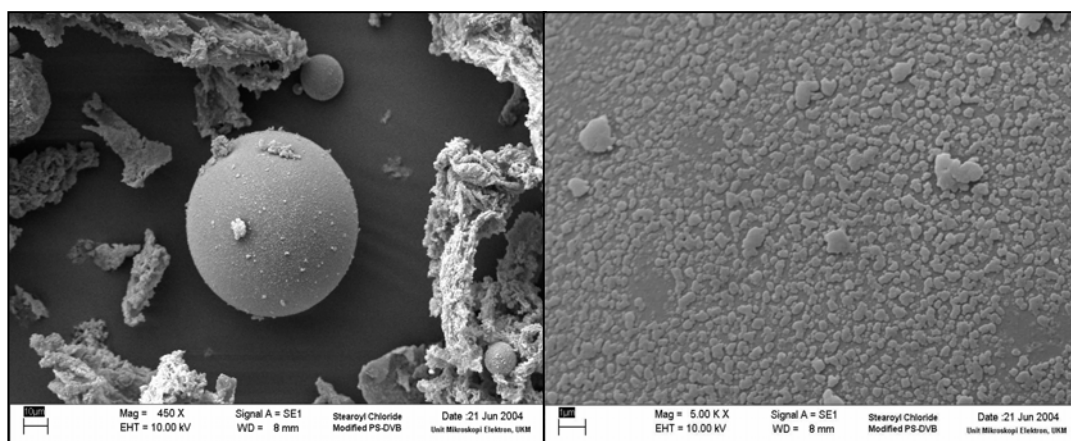


**Figure 4.17** The Infrared Spectra of Modified PS-DVB: (a) Chloromethyl PS-DVB, (b) Octadecyloxy Methyl PS-DVB

#### 4.4.2 Characterization of modified PS-DVB by Scanning Electron Microscopy

The scanning electron microscopy (SEM) is a technique that uses electrons rather than light to form an image. The SEM also produces images of high resolution, which means that closely spaced features can be examined at high magnification. The surface morphology and particle size of PS-DVB heptadecyl ketone prepared based on Friedel-Crafts, chloromethyl PS-DVB by using chloromethylation, and octadecyloxy methyl PS-DVB prepared based on Williamson ether reaction are shown in Figure 4.18, Figure 4.19 and Figure 4.20, respectively.

Figure 4.18a illustrates that the particle morphology of PS-DVB heptadecyl ketone was spherical beads. It was found that the average particle size of PS-DVB heptadecyl ketone was 60  $\mu\text{m}$ . The PS-DVB heptadecyl ketone displayed the presence of impurities that probably from the acylation agent during the acylation reaction process. The PS-DVB heptadecyl ketone is performing the image of yellow brownies powder, chemically stable, mechanically strong, and easily functionalized. From the Figure 4.18b illustrated that the surface morphology of PS-DVB heptadecyl ketone was heterogeneous, roughly, and the surface morphology looks like gravel.



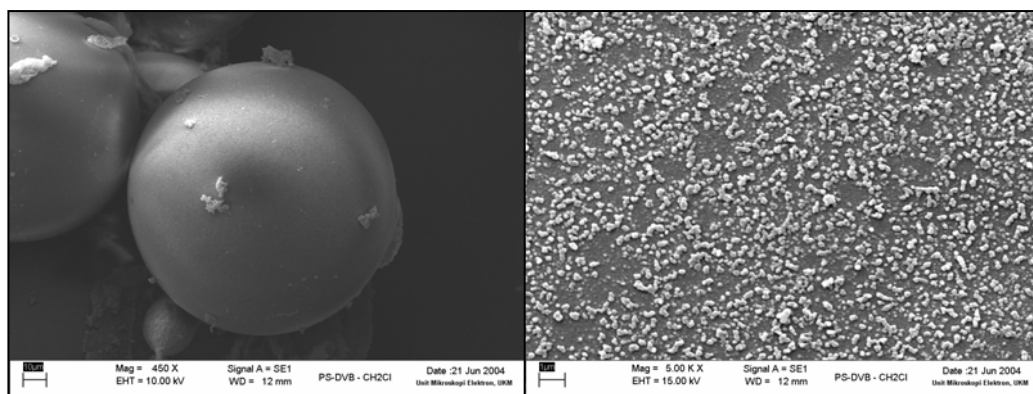
(a). Magnification was 450  $\times$

(b). Magnification was 5.0 K  $\times$

**Figure 4.18** SEM Micrographs of PS-DVB Heptadecyl Ketone Prepared Based on Friedel-Crafts Acylation

The SEM micrograph of chloromethyl PS-DVB (Figure 4.19a) shows that the particles of Chloromethyl PS-DVB were globular beads. Apparently, there were some impurities on the surface particle. The surface morphology of chloromethyl PS-DVB (Figure 4.19b) appeared heterogeneous and rough.



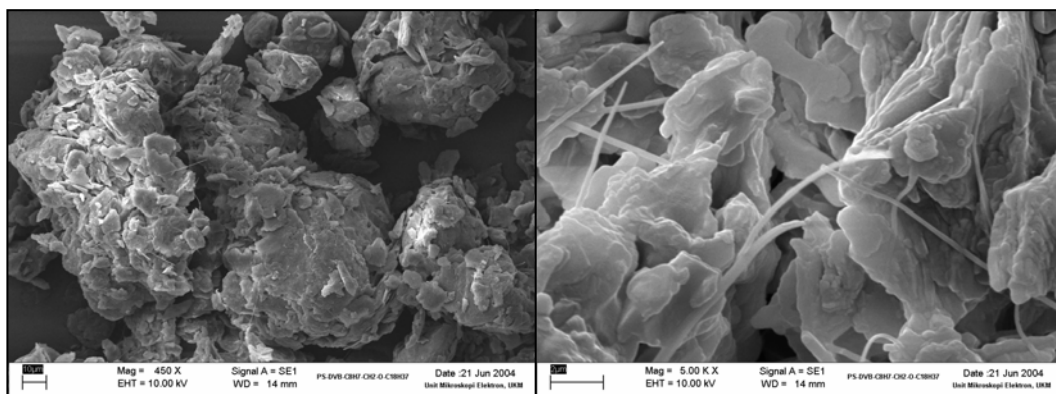


(a). Magnification was 450 ×

(b). Magnification was 5.0 K ×

**Figure 4.19** SEM Micrographs of Chloromethyl PS-DVB by Using Chloromethylation

The Figure 4.20a shows that the particle morphology of the octadecoxy methyl PS-DVB was different compare to other micrographs. The particle morphology of the octadecoxy methyl PS-DVB looks like rocky, whereas its surface is rough and irregular shape beads, not well formed. The average particle size of octadecoxy methyl PS-DVB is 32  $\mu\text{m}$ . The synthetic octadecoxy methyl PS-DVB was pale yellow, like wax, unstable with the temperature, when the temperature is higher ( $>25^{\circ}\text{C}$ ), the octadecoxy methyl PS-DVB melted. The higher temperature had broken the linkage ether (C-O-C). It shows some irregular agglomerates.



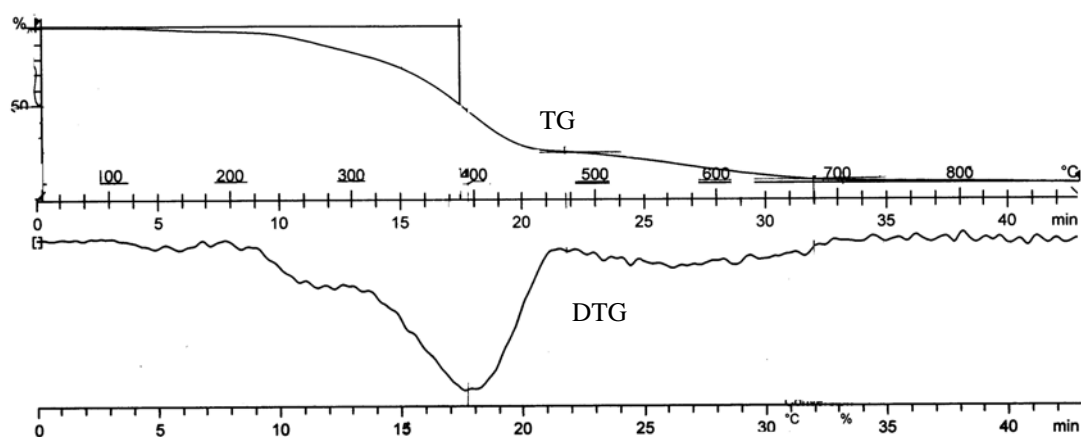
(a). Magnification was 450 ×

(b) Magnification was 5.0 K ×

**Figure 4.20** SEM Micrographs of Octadecoxy Methyl PS-DVB Prepared Based on Williamson Ether Reaction

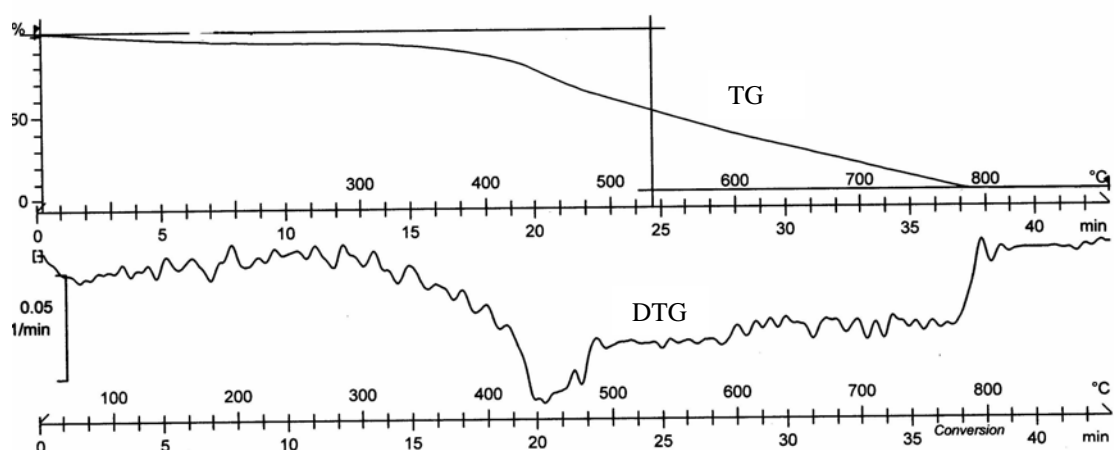
#### 4.4.3 Characterization by Thermogravimetry (TG) and Derivative Thermogravimetry (DTG)

Thermogravimetric analysis was carried out in order to establish the stability of the adsorbents and the results can be used in environmental analysis. Figure 4.21 shows TG and DTG thermograms for octadecoxy methyl PS-DVB. A sharp weight loss was observed over the temperature range 230-520°C in a similar manner to that observed in the thermograms for the chloromethyl PS-DVB. The total weight loss over this temperature range (520-900°C) is 12.33% of the initial sample weight and this can be attributed to the elimination of more stable organic compounds and from decomposition of the ether group.



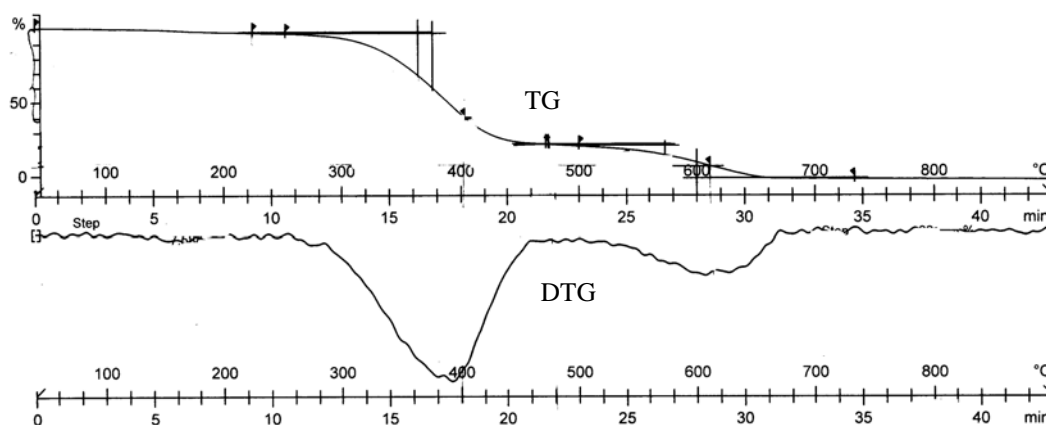
**Figure 4.21** TG and DTG Thermograms for Octadecoxy Methyl PS-DVB

The total weight loss for the PS-DVB heptadecyl ketone is 97.26% of the initial sample weight and this was probably mainly due to the complete loss of adsorbed and coordinated water from sample together with the loss of some carbonyl functional groups. The PS-DVB heptadecyl ketone still left a residue as much as 2.74%.



**Figure 4.22** TG and DTG Thermograms for PS-DVB Heptadecyl Ketone

The thermal degradation of chloromethylated PS-DVB derivatives takes place in three stages with different weight losses depending on the nature of the substituents. The octadecoxy methyl is less thermal stability compare to chloromethyl PS-DVB PS-DVB, and PS-DVB heptadecyl ketone. Because the thermal stability both of them were same in the room temperature, but when the temperature was increased, the thermal degradation of constituents of octadecoxy methyl PS-DVB was first degraded at 230°C, and the weight loss percentage of compounds most highest. The Figure 4.23 illustrated that the thermogravimetric thermogram for chloromethyl PS-DVB nearly similar with that of home-made PS-DVB. The derivative thermogravimetric thermogram of the chloromethyl PS-DVB indicates occurrence of two peaks. The two peaks have different stability. The first peak was observed at 400°C, and the second peak appeared at 620°C. The both of these peaks were different because the occurrence of two functional groups in the different thermal stability.



**Figure 4.23** TG and DTG Thermograms for Chloromethyl PS-DVB

The characteristics obtained from thermogravimetric analysis and derivative thermogravimetric analysis of PSDVB and the modified PS-DVB (PS-DVB heptadecyl ketone, chloromethyl PSDVB, and octadecoxy methyl PSDVB) are presented in Table 4.7. The complexity of the thermal decomposition for chemically modified polymers can be easily noted from the thermogravimetric thermograms. The substitution at the benzene ring of PS-DVB determines three degradation stages with different weight losses depending on the chemical structure of the substituents. From the Table 4.7 it is apparent that the most important weight loss was recorded in the last stage of thermal degradation of the PS-DVB and modified PS-DVB in the temperature range of 230-520°C.

**Table 4.7:** The Thermogravimetric Data for Native PS-DVB and Modified PS-DVB

Sample	Weight loss (Wt%) and temperature range(T°C) for the three stages degradation		
	Stage I 40-230°C	Stage II 230-520°C	Stage III 520-900 °C
PS-DVB (native)	4.54%	85.33%	10.13%
PS-DVB heptadecyl ketone	6.49%	38.64%	52.13%
Chloromethyl PS-DVB	3.95%	77.38%	18.67%
Octadecoxy methyl PS-DVB	4.35%	79.58%	16.07%

From the results obtained, it can be concluded that the thermal stability decreases in the order: PS-DVB heptadecyl ketone > chloromethyl PS-DVB > octadecyloxy methyl PS-DVB > PS-DVB. The results also showed that the PS-DVB heptadecyl ketone is the most stable whereas the PS-DVB has the highest degradation rate in the considered temperature range.

## **CHAPTER 5**

### **APPLICATION OF PS-DVB AND MODIFIED PS-DVB IN SOLID PHASE EXTRACTION**

#### **5.1 Introduction**

This chapter presents and discusses the experimental data obtained in chemical characterization of the adsorbents through solid phase extraction (SPE) analysis.

Gas chromatography (GC) is one of the most widely employed analytical techniques today. The wide acceptance and success of this technique have been due to such features as simplicity, rapidity of analysis, high sensitivity of detector systems, efficiency of separations, varied applications, and the use of very small samples (microgram or smaller). Presently GC is finding use in the concentration of impurities in the parts per million (ppm) and parts per billion (ppb) ranges and in addition to the actual measurement of impurities at these levels. Without the use of GC, many analytical problems could not be solved or would involve more intricate and time-consuming techniques [59].

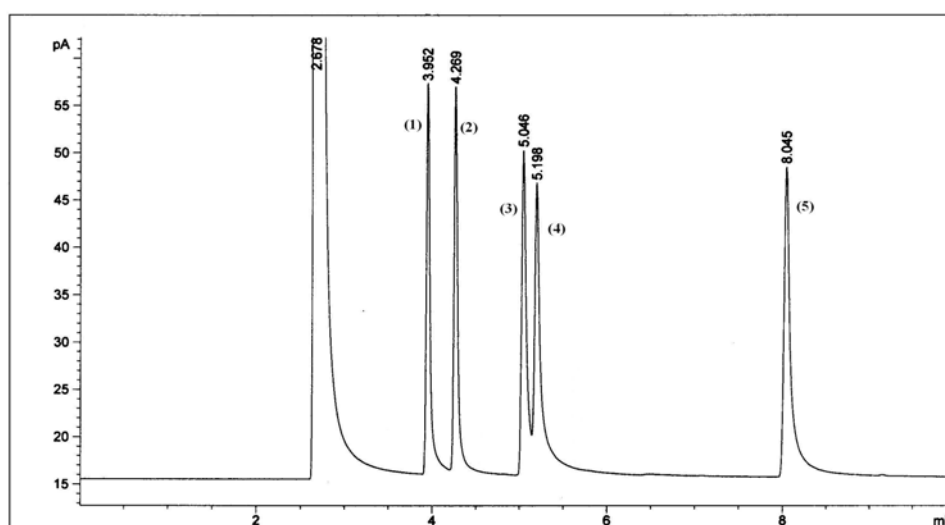
SPE is selected due to its inherent advantages such as ease of maintenance and automation, time and cost saving, and prevention of emulsion formation [17]. The principle of SPE is similar to liquid - liquid extraction involving a partitioning of compounds between two phases. Objectives that can be possibly achieved on SPE are removal of interfering compounds, pre-concentration of sample, and fractionation of the sample into different compounds or group of compounds as in classical chromatography. It also promotes storage of analytes that are unstable in a liquid medium. Therefore, the SPE process can be carried out either on-line or off-line. The experimental procedure using the SPE cartridges is known as offline SPE.

The adsorbents used in the research were home-made PS-DVB, PS-DVB heptadecyl ketone, chloromethyl PS-DVB, and octadecyloxy methyl PS-DVB. These adsorbents were compared with commercial adsorbents, namely commercial PS-DVB, and octadecyl silane bonded silica. The efficiency of the adsorbents that utilized in SPE can be easily determined by examining the percentage recovery for various test compounds. The concentrations and the percentage recovery for each test compound were calculated using the equations given in 3.3 and 3.4 (Chapter 3).

## **5.2 Identification of Peaks for Test Compounds and Internal Standard**

In this research, gas chromatography was chosen as the separation and quantitative techniques for the solid phase extraction recovery study of the adsorbents. The test compounds used in this research were benzaldehyde, 2-chlorophenol, *p*-cresol and nitrobenzene. Butyrophenone was chosen as the internal standard. Identification of each analyte was carried out by comparison of retention times in chromatogram with standards.

A mixture solution of all the test compounds and butyrophenone (2000 ppm) were prepared by diluting the stock solutions in methanol. The mixture (1  $\mu$ L) was then injected into a gas chromatograph. A chromatogram obtained is shown in Figure 5.1. The retention time for each individual test compound was determined by injecting 1  $\mu$ L of each stock solution prepared into the gas chromatograph. All the test compounds and butyrophenone were separated by gas chromatography in less than ten minutes. The retention times for the test compounds as well as the internal standard are listed in Table 5.1. The gas chromatograms obtained for the test compounds and butyrophenone are shown in Appendices A1-A5.



**Figure 5.1** Separations of Test Compounds and Butyrophenone (Internal Standard) Using Gas Chromatography. Chromatographic Condition: Ultra-1 Column (30 m  $\times$  250  $\mu$ m  $\times$  0.20  $\mu$ m), Carrier Gas: Helium; Flow Rate: 1.1 mL/min; Pressure: 75 kPa; Detector: FID; Injector Temperature: 250°C; Detector Temperature: 310°C; Initial Temperature: 100°C with a Hold Time of 2 min; Final Temperature: 140°C, Linear Temperature Programmed at 5°C/min rise. Peaks: **1** – Benzaldehyde; **2** – 2-Chlorophenol, **3** – *p*-Cresol, **4** – Nitrobenzene, **5** – Butyrophenone



**Table 5.1:** Retention Time of the Test Compounds and Butyrophenone in GC Chromatogram

Compound	Retention time, ( $t_R$ /minutes)
Benzaldehyde	3.95
2-Chlorophenol	4.27
<i>p</i> -Cresol	5.05
Nitrobenzene	5.20
Butyrophenone (Internal Standard)	8.05

### 5.3 Determination of Response Factor for Test Compounds and Internal Standard

The response factor is usually utilized in GC quantification calculation. This is because the response factor can significantly eliminate several errors that are usually observed in GC analysis. In this study, 1  $\mu$ L of each test compound and the internal standard stock solutions in concentration of 100,000 ppm was injected into the gas chromatograph to determine the response factor ( $F_x$ ) for each compounds. Triplicate injections were carried out to obtain a more accurate data. The response factors for each compound were calculated using equations 3.2 given in Section 3.7. Table 5.2 shows the peak area, average peak area, and response factor for each of the analytes examined in this study.

**Table 5.2:** Peak Area, Average Peak Area, and Response Factor of Test Compounds and Internal Standard

Compound	Peak Area (pA.s)			Average Peak Area (pA.s)	Response Factor
Benzaldehyde	1204	1524	1639	1456	0.0146
2-Chlorophenol	1026	853	1255	1045	0.0104
<i>p</i> -Cresol	1883	1798	1366	1682	0.0168
Nitrobenzene	1401	1160	1806	1456	0.0146
Butyrophenone (IS)	1486	1695	1319	1500	0.0150

#### 5.4 Efficiency of Home-made PS-DVB, PS-DVB Heptadecyl Ketone, and C<sub>18</sub>-Silica Adsorbents

The efficiency of PS-DVB, and PS-DVB heptadecyl ketone, PS-DVB and C<sub>18</sub>-silica in SPE were investigated using various test compounds under individual and simultaneous extraction conditions. The performances of the home-made PS-DVB, PS-DVB heptadecyl ketone, and C<sub>18</sub>-silica were determined by the means of percentage recovery of test compounds. In order to point out the statistical difference of these results, *t*-test was evaluated at a confidence level of 95%. The evaluation of the statistical test was determined by using the formula given in Section 3.5.6. Table 5.3 shows the comparison of recovery percentages and relative standard deviation (R.S.D) values obtained using home-made PS-DVB, PS-DVB heptadecyl ketone, and C<sub>18</sub>-silica adsorbents. The calculation of concentrations and the percentages recovery of the test compounds are shown in Appendix B.

Based on the results obtained in Table 5.3, it was observed that the best recoveries were achieved for all the test compounds using C<sub>18</sub>-silica as adsorbent. Meanwhile, the recoveries obtained using home-made PS-DVB and PS-DVB heptadecyl ketone were slight lower in relative with C<sub>18</sub>-silica. However, the PS-DVB heptadecyl ketone showed an overall increase of recovery for all the test compounds compared to the home-made PS-DVB.

**Table 5.3:** Comparison of Percentages of Recovery and Relative Standard Deviation for the Extraction of Test Compounds Using Home-made PS-DVB, PS-DVB Heptadecyl Ketone, and C<sub>18</sub>-silica as the Adsorbents

Compound	home-made PS-DVB				PS-DVB heptadecyl ketone				C <sub>18</sub> -silica			
	Individual extraction		Mixture extraction		Individual extraction		Mixture extraction		Individual extraction		Mixture extraction	
	% R	RSD (%)	% R	RSD (%)	% R	RSD (%)	% R	RSD (%)	% R	RSD (%)	% R	RSD (%)
Benzaldehyde	55.74	1.58	41.85	9.25	63.63	3.71	67.09	4.04	69.86	4.07	85.77	3.71
2-Chlorophenol	44.33	4.39	15.81	8.50	82.70	6.30	65.30	4.28	83.87	4.26	89.21	6.30
<i>p</i> -Cresol	30.29	5.60	7.41	4.10	46.68	5.06	35.16	3.46	66.67	3.94	72.11	5.06
Nitrobenzene	64.02	5.42	71.01	4.95	69.15	2.67	79.39	2.65	86.42	3.54	76.35	2.67

According to the literature [40, 60], if the adsorbent packing process in SPE tube is less efficient, it will cause the formation of empty space among the adsorbent particles in the tube. The formation of this empty space will decrease the surface area of the adsorbent that interact with the analytes, subsequently reduce the efficiency of the adsorption, and desorption of the adsorbent. Adsorbent with large particle size will also significantly decrease its surface area and lead to poor recovery percentages of test compounds. In order to avoid this phenomenon, home-made PS-DVB was ground and sieved to 400 mesh (38  $\mu\text{m}$ ). A total of approximately 500 mg of the adsorbent was loaded into the SPE tube to form a bed of 1 cm  $\times$  1.5 cm I.D. A bed height of more than 1 cm should be used to ensure good retention of the desired sample compounds [48]. The resin was closely packed, because loose-packed resin bed will cause the channeling of the analytes that can lead to poor recoveries.

Loosely packed adsorbent will also result in uncontrollable flow rate when the SPE was carried out. In SPE system, the flow rate of the sample solution is one of the most important parameters, which not only affects the recoveries of analytes, but also controls the time of analysis [61]. Ersöz, *et al.* [62] reported that the adsorption of analytes decreases with increasing flow rate. At higher flow rates, the contact time of analytes with the adsorbent is short. Thus, the mass transport of the analytes to the reactive sites of the adsorbent will reduce and decrease the retention of the analytes. The home-made PS-DVB sorbent was closely packed in the tube, a flow rate of approximately 1 mL/min was used to ensure the interaction between the analytes, and adsorbent was sufficient and achieved good recoveries of the test compounds.

The low recoveries of PS-DVB might also be due to the hydrophobic surface of the polymer. The consequence is poor surface contact with predominantly aqueous solutions. Pretreatment of the PS-DVB with an activating solvent (methanol) must be carried out to obtain better surface contact with the aqueous solution being extracted. However, sometimes the activating solvent can gradually leach out of the resin, causing the extraction to become ineffective [47]. As for PS-DVB heptadecyl ketone, the hydrophilic character of the introduced functional groups increased its surface polarity and improved the adsorbent wetting property. It was due to the ability of polar surface to reduce the surface tension of the water that enabled the aqueous sample to interact with the resin surface and enhanced the mass transfer of the

analytes from the water solution to the sorbents and resulted in higher recovery [3, 63, 43, 39].

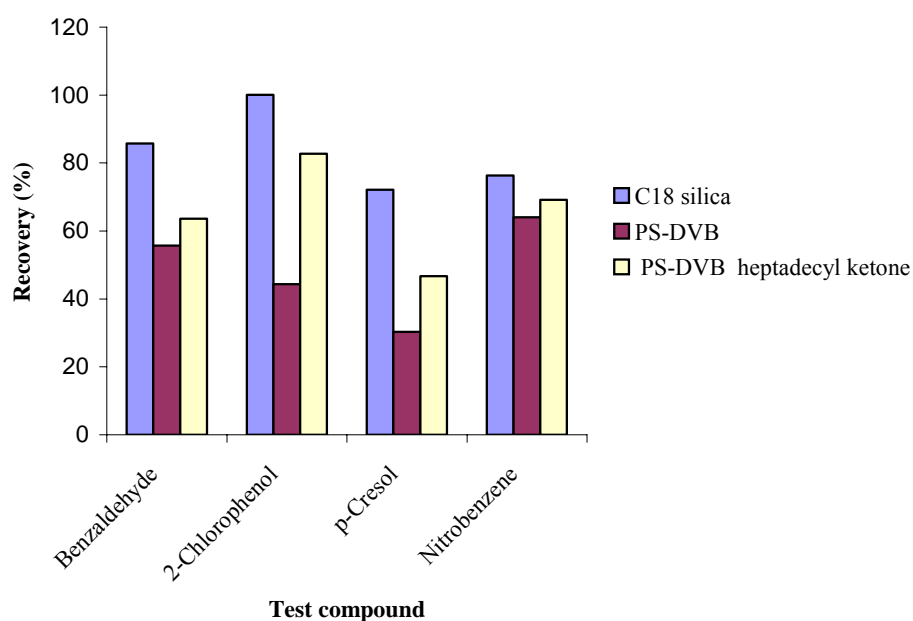
For PS-DVB heptadecyl ketone, the recoveries were generally higher than PS-DVB because the presence of the carbonyl groups on its surface allowed better interaction with the methanol. On the other hand, ethyl acetate, acetonitrile, and tetrahydrofuran were highly recommended and reported to be the suitable elution solvent for PS-DVB and derivatized PS-DVB compared to methanol [8, 40, 47, 13]. Similar observations had also been reported by Schmidt *et al.* [48] in which the recoveries for *p*-cresol was the highest using acetyl-PS-DVB (94%), followed by underivatized PS-DVB (76%) and C<sub>18</sub>-silica (19%) when ethyl acetate was used as the elution solvent.

PS-DVB heptadecyl ketone appeared to show significantly higher recoveries with lower RSD values for all the test compounds tested compared to home-made PS-DVB. These results were well expected because chemical modifications of the PS-DVB with stearyl groups had improved the efficiency of the SPE process by increasing polar interactions with the functional groups of the analytes and thus resulted in higher retention [3, 19, 29]. Similar observations had also been reported by Masqué, *et al.* [5] on solid phase extraction of pesticides and phenolic compounds from water.

The main reason why highest recoveries were achieved for all test compounds using C<sub>18</sub>-silica was attributed to the type of elution solvent used in our research. The elution sample should be allowed that the analytes always involves the primary and secondary retention mechanisms between the analytes and adsorbent and the elution solvent utilized should be compatible with the final analysis technique too. Hence, in this experiment, methanol was chosen as the elution solvent because it was less toxic compared to other solvent such as acetonitrile [13] and its volatile characteristic was compatible to the subsequent gas chromatography analysis. According to previous reports [40, 53, 64], methanol was found to be a good elution solvent for the extraction of polar compounds using octadecyl silica adsorbents. This was probably due to the hydroxyl group on methanol that

contributed to its polarity and enabled the solubility of analytes retained in the C<sub>18</sub>-silica adsorbent.

The two dimensional illustration (Figure 5.2) shows the percentage recovery of test compounds under individual and simultaneous extraction using home-made PS-DVB, PS-DVB heptadecyl ketone, and C<sub>18</sub>-silica as adsorbent. The overall results demonstrated high recoveries in the range of 67% - 99% using the C<sub>18</sub>-silica as an adsorbent. However, lower recoveries in the range of 30%-99% were obtained when the home-made PS-DVB used as the adsorbent.



**Figure 5.2** Percentages of Recovery for Test Compounds Extracted Individually Using Home-made PS-DVB, PS-DVB Heptadecyl Ketone, and C<sub>18</sub>-silica as the Adsorbents

## 5.5 Hypothesis Test

The examples of the hypothesis test calculation for benzaldehyde under individual extraction using PS-DVB heptadecyl ketone and home-made PS-DVB as the adsorbents is shown below:

Null hypothesis,  $H_0 = \mu_1 - \mu_2 = \mu_0 = 0$

Alternative hypothesis,  $H_1 = \mu_1 - \mu_2 > 0$

Level of significance,  $\alpha = 0.05$

$$t_{\text{test}} = \frac{X_1 - X_2 - \mu_0}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

$$t_{\text{test}} = \frac{63.63 - 55.74 - 0}{\sqrt{\frac{2.5060^2}{9} + \frac{0.9324^2}{9}}}$$

$$t_{\text{test}} = \frac{7.89}{0.8913}$$

$$= 8.8522$$

$$\text{Degree of freedom, } v = \frac{\left( \frac{s_1^2}{n_1} + \frac{s_2^2}{n_2} \right)^2}{\frac{\left( \frac{s_1^2}{n_1} \right)^2}{n_1 - 1} + \frac{\left( \frac{s_2^2}{n_2} \right)^2}{n_2 - 1}}$$

$$\text{Degree of freedom, } v = \frac{\left( \frac{2.5060^2}{9} + \frac{0.9324^2}{9} \right)^2}{\frac{\left( \frac{2.5060^2}{9} \right)^2}{9 - 1} + \frac{\left( \frac{0.9324^2}{9} \right)^2}{9 - 1}}$$

$$\text{Degree of freedom, } \nu = \frac{0.6310}{0.0620} \approx 10$$

$$t_{0.05,10} = 2.23$$

From the calculations, it was shown that  $t_{\text{test}} > t_{0.05,10}$ . Therefore,  $H_0$  was rejected and  $H_1$  was accepted where  $\mu_1 > \mu_2$ . This represented that PS-DVB heptadecyl ketone proved to give higher percentage recovery than home-made PS-DVB.

## 5.6 Measurement of Breakthrough Volume

The efficiency of unmodified PS-DVB and modified PS-DVB can also be determined by measuring the breakthrough volume of the adsorbents. The breakthrough volume of the adsorbent was calculated by using the equation 3.11 and 3.12 in section 3.5.7. In this research, frontal analysis was performed by pumping a dilute solution of the analyte (nitrobenzene and 2-chlorophenol) through the adsorbent bed and examined the detector response as a function of time. The concentration of the analyte was prepared in 20 ppm in all cases studied. Table 5.4 showed the breakthrough volume of unmodified and modified PS-DVB sorbents using different types of test compounds. The calculation of breakthrough volume is shown in Appendix B3.

**Table 5.4:** Breakthrough Volume of Unmodified and Modified PS-DVB Sorbents Using Different Types of Analytes

Code Sample	Nitrobenzene 20 ppm		2-Chlorophenol 20 ppm	
	Average breakthrough volume (mL)	RSD (%)	Average breakthrough volume (mL)	RSD (%)
PS-DVB	13.40	7.46	13.60	15.56
PS-DVB heptadecyl ketone	30.60	11.56	20.47	7.59
Chloromethyl PSD-VB	1.23	18.72	2.07	13.32
Octadecoxy methyl PS-DVB	1.03	12.37	1.00	20.00

The breakthrough volumes for PS-DVB heptadecyl ketone was significantly higher compared to those observed using other modifiers and unmodified PS-DVB. The results (Table 5.4) indicate that the highest breakthrough volume for nitrobenzene was obtained using PS-DVB heptadecyl ketone (30.60 mL), followed by unmodified PS-DVB (13.40 mL), chloromethyl PS-DVB (1.23 mL), and octadecoxy methyl PS-DVB (1.03 mL) as the adsorbent. In addition, higher breakthrough volume was observed for PS-DVB heptadecyl ketone when lower polarity analyte such as nitrobenzene (30.60mL) compared to the more polar 2-chlorophenol (20.47 mL). These observations were similar to those described in the literature [39], which reported that the retention volume and breakthrough volume for the nitrobenzene was higher than the retention volume and breakthrough volume for the more polar 2-chlorophenol using PS-DVB heptadecyl ketone. The PS-DVB heptadecyl ketone is a resin that contains stearyl chloride functional groups attached to the benzene rings that alter the PS-DVB heptadecyl ketone retentive properties for polar compounds. The incorporation of stearyl groups on PS-DVB improved the efficiency of the adsorbent by increasing the ability of the adsorbent to undergo polar interactions with the polar analytes. Higher surface area on the stearyl chloride-modified PS-DVB adsorbent allocated higher interactions between solutes and adsorbent and yielded higher retention of analytes. In addition, the presence of the polar carbonyl groups on its surface that allowed better contact with solvent.

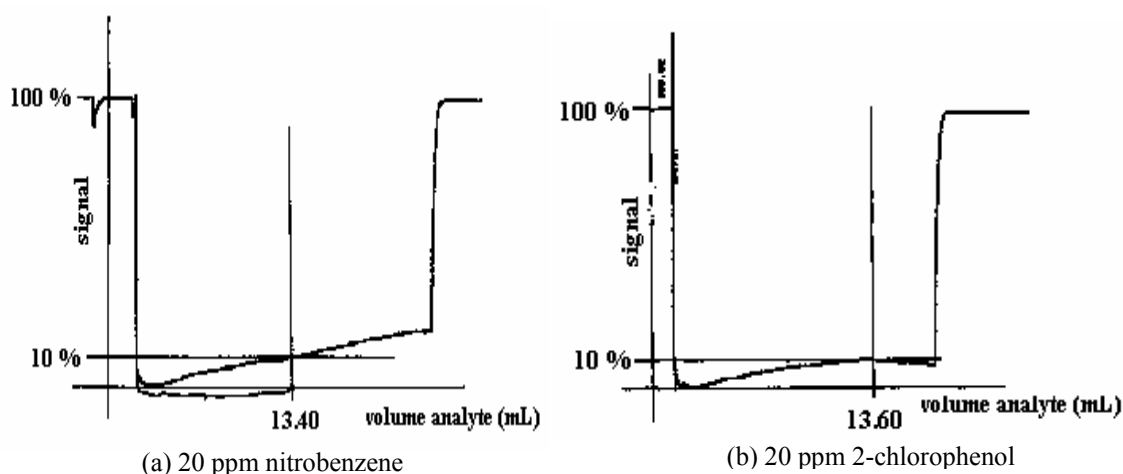
According to the acid-base Lewis theory, the benzene rings on PS-DVB and the carbonyl group on PS-DVB heptadecyl ketone can be considered as a Lewis base while the phenolic compounds (2-chlorophenol) can act as a Lewis acid. However, the oxygen on the carbonyl group on PS-DVB heptadecyl ketone exhibited larger dipole moment and resulted in better Lewis base property in relative with the benzene ring on PS-DVB. Consequently, the interaction of phenolic compounds was found to be much better by using PS-DVB heptadecyl ketone instead of PS-DVB adsorbent.

Another possibility that lead to higher breakthrough volume when using PS-DVB heptadecyl ketone compared to PS-DVB is the porosity and surface area of the modified adsorbent. PS-DVB heptadecyl ketone is expected to be more porous and has a relatively smaller pore size and higher surface area compared to the unmodified



PS-DVB. Higher or larger specific surface area had been reported to allow stronger retention of analytes than the conventional polymeric adsorbents. [65, 66]. Increase in the specific surface area of the adsorbent will allow additional  $\pi$ - $\pi$  interactions between the solutes and the adsorbents [43]. Sun and Fritz [47] reported that the surface area and porosity of resins seem to have a major effect on their efficiency for SPE.

Breakthrough volume curves for nitrobenzene and 2-chlorophenol using PS-DVB as the adsorbents are illustrated in Figure 5.3. Based on the results, it was found that the used of PS-DVB as adsorbent generally resulted in lower breakthrough volume when compared to PS-DVB heptadecyl ketone adsorbent. This might be due to the Van der Waals and/or hydrophobic interactions between the solutes and the adsorbent that affected the extraction of aromatic compounds [67].



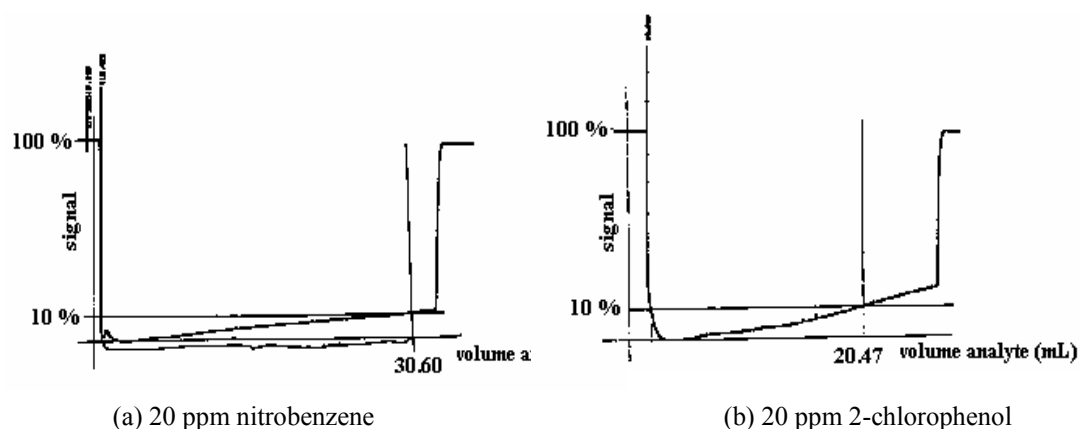
**Figure 5.3** Breakthrough Volume Curves for (a) Nitrobenzene and (b) 2-Chlorophenol Using PS-DVB as the Adsorbent

Based on the previous report [68], the retention mechanisms on the PS-DVB will differ depending on the nature of analytes and the basic mechanisms were found to involve  $\pi$ -interactions and dispersive interactions. The analyte  $\pi$ -systems and the adsorbent  $\pi$ -electron donating-accepting fragments usually play an important role in determining the retention mechanism. PS-DVB possesses exceptionally strong  $\pi$ -electron donating-accepting ability, which causes a predominant retention of

compounds that contain aromatic  $\pi$ -systems or functional groups with lone electron pairs such as carbonyl and nitro groups.

Previous report [68] also demonstrated an interesting regularity in the retention of mono-, bi- and trisubstituted benzenes on polystyrene. The retention increased with an increase of  $\pi$ -electron density gradients in molecules, which are usually known as local dipoles. The electron resonance structures of the analyte molecules were found to be applicable for the estimation of their retention. Retention of bi- and trisubstituted benzenes on polystyrene was poorer than the monosubstituted benzenes because in bi- and tri-substitution, the magnitude of the resonance effect was poorer, thus resulted in minimum local  $\pi$ -electron density dipoles. Therefore, in our study, it can be seen that 2-chlorophenol (bisubstituted benzene) was less retained in relative with nitrobenzene (monosubstituted benzene) on the PS-DVB adsorbent.

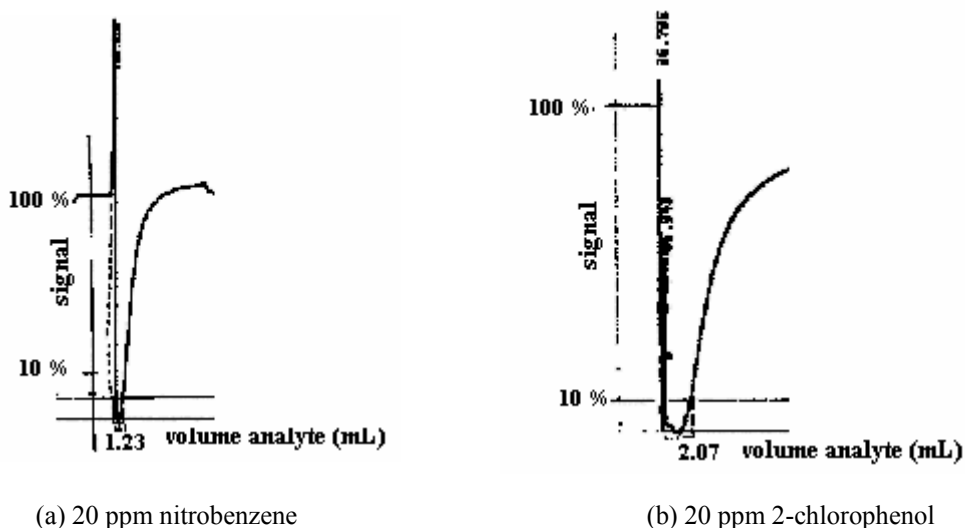
Breakthrough volume curve of nitrobenzene and 2-chlorophenol using PS-DVB heptadecyl ketone as the adsorbent is illustrated in Figure 5.4. Based on the results in Table 5.4, the use of PS-DVB heptadecyl ketone as adsorbent generally resulted in higher breakthrough volume when compare to PS-DVB adsorbent. In addition, breakthrough volumes for more polar compounds were generally lower than the breakthrough volumes for less polar compounds using PS-DVB heptadecyl ketone as adsorbent. 2-Chlorophenol predicted to be retained on the adsorbent via primary interaction that involved the hydrogen bonding between the hydrogen from hydroxyl groups of the analyte and the oxygen from the carbonyl groups on the adsorbent.



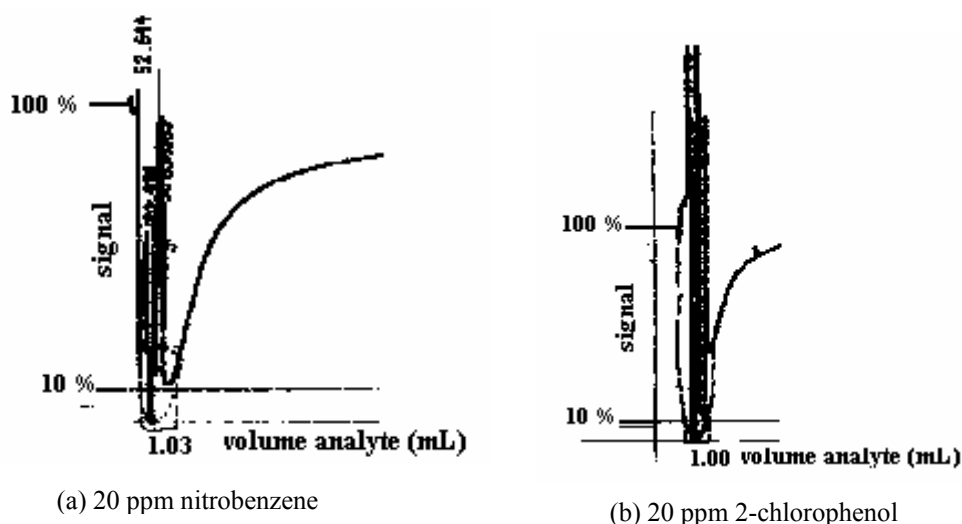
**Figure 5.4** Breakthrough Volume Curves of (a) Nitrobenzene and (b) 2-Chlorophenol Using PS-DVB Heptadecyl Ketone as the Adsorbent

In general, the breakthrough volumes were much better for nitrobenzene compared to 2-chlorophenol on PS-DVB heptadecyl ketone adsorbent. Significant improvement was observed when non-polar compound, nitrobenzene achieved higher breakthrough volume on modified PS-DVB sorbent in relative with native PS-DVB. The polymer can act as an electron donor for analytes having electron-withdrawing or positive electron resonant capacity substituents. The degree of cross-linking for the copolymer is also an important parameter that can explain the differences in breakthrough volume among the adsorbents.

From Figure 5.5 and Figure 5.6, it was observed that the breakthrough volume for chloromethyl PS-DVB and octadecoxy methyl PS-DVB were almost identical. For chloromethyl PS-DVB adsorbent, the breakthrough volumes of nitrobenzene and 2-chlorophenol as analytes were 1.23 mL, and 2.07 mL, respectively, while for octadecoxy methyl PS-DVB the values were 1.03 mL and 1.00 mL, respectively.



**Figure 5.5** Breakthrough Volume Curves of (a) Nitrobenzene and (b) 2-Chlorophenol Using Chloromethyl PS-DVB as the Adsorbent.



**Figure 5.6** Breakthrough Volume Curves of (a) Nitrobenzene and (b) 2-Chlorophenol Using Octadecoxy Methyl PS-DVB as the Adsorbent.

The unsatisfactory breakthrough volumes for chloromethyl PS-DVB and octadecoxy methyl PS-DVB adsorbents were mostly attributed to the elution solvent used in our study. The octadecoxy methyl PS-DVB has been shown to lack of selectivity on polar compounds such as 2-chlorophenol and less polar compound such as nitrobenzene.

In this research, a new method based on Williamson ether reaction was used to modify PS-DVB. The applicability of octadecoxy methyl PS-DVB adsorbent was the major interest in our current study. Nevertheless, the adsorbent have shown unsatisfactory breakthrough volumes and poor percentage recovery compared to other modified adsorbent such as PS-DVB heptadecyl ketone and chloromethyl PS-DVB. The main reason why octadecoxy methyl PS-DVB adsorbent did not give an expected high performance could be due to the incomplete preparation of octadecoxy methyl PS-DVB. Hence, in the future study, the preparation should be improved in order to avoid the presence of any impurities that will affect the efficiency of the modified material when utilized as an adsorbent. The poor performance of synthesized octadecoxy methyl PS-DVB could also probably due to the irregular shape of the adsorbent particles as shown in Figure 4.20, as compare to spherical shape particles of PS-DVB (Figure 4.3) and PS-DVB heptadecyl ketone (Figure 4.18). Spherical shaped adsorbents can be packed tightly, less channeling, and give higher efficiency packing

## CHAPTER 6

### CONCLUSIONS AND SUGGESTIONS

#### 6.1 Conclusions

In this study, PS-DVB adsorbents have been successfully synthesized and modified via three different methods. The effects of reaction time and type of stirrer used for the polymerization were studied in order to obtain suitable set of conditions for PS-DVB adsorbents with excellent physical properties. The optimum reaction time for polymerization was for 15 h at 80°C. The results have showed that cross-blade impeller stirrer gave a particle size of PS-DVB approximately 74  $\mu\text{m}$ . According to the nitrogen adsorption characterization, the use of a cross-blade impeller stirrer gave a smaller average pore diameter (38.40 Å) compared to a half-moon impeller (183.58 Å) and a double cross blade impeller (76.19 Å). The reaction time indicated that 15 h gave a larger average pore diameter (300.42 Å) compared with those for 1 h (35.33 Å), 5 h (76.19 Å), 10 h (163.59 Å), and 20 h (65.08 Å).

The surface characteristics of unmodified PS-DVB and modified PS-DVB adsorbents, i.e. PS-DVB heptadecyl ketone, chloromethyl PS-DVB, and octadecoxymethyl PS-DVB were determined by using fourier transform infrared spectrofotometry, scanning electron microscopy, thermogravimetric analysis, nitrogen adsorption analysis. In general, the modified PS-DVB adsorbents were mesoporous.

The FTIR spectra for home-made PS-DVB (unmodified) were similar to the FTIR spectra of the commercial PS-DVB suggesting that the home-made PS-DVB has the same structural properties as the commercial PS-DVB. As for PS-DVB heptadecyl ketone, the FTIR analysis showed a carbonyl band at  $1684.7\text{ cm}^{-1}$  which was related to ketonic (C=O) stretching. This indicated the incorporation of the stearyl functional groups to the PS-DVB. Meanwhile, the similarities between the spectra of commercial PS-DVB, home-made PS-DVB and PS-DVB heptadecyl ketone also suggested that the basic structural units of PS-DVB were preserved in the polymer.

The SPE efficiencies of the home-made PS-DVB, PS-DVB heptadecyl ketone adsorbents and C<sub>18</sub>-silica, were determined by means of percentage recovery of test compounds. Excellent recoveries of more than 70% and good reproducibility (R.S.D. between 2% and 7%) were obtained using C<sub>18</sub>-silica as the adsorbent. When all the test compounds were extracted simultaneously by C<sub>18</sub>-silica as the adsorbent, average recoveries were between 69% and 87% and low relative standard deviation (R.S.D. between 3% and 4%) were achieved. Overall, both individual and mixture extractions yield higher recoveries for the compounds of lower polarity, nitrobenzene and benzaldehyde compared to the more polar compound, *p*-cresol with the lowest percentage of recovery. This was attributed to the non-polar nature of the C<sub>18</sub>-silica that favours the non-polar interaction between the less polar analytes and the adsorbent. The only exception was for 2-chlorophenol. It is a more polar compound but has the highest percentage of recovery due to the accessibility of the analyte to the polar silanol group of the adsorbents resulted in the hydrogen bonding (between the analyte and the adsorbents, the polarity of the elution solvent used). 2-Chlorophenol was the first compound extracted by the newly packed C<sub>18</sub>-silica SPE

tube as there are no interferences present in the newly packed adsorbent, thus yield higher recovery.

For the home-made PS-DVB, the recoveries for all the four phenolic and substituted aromatic compounds that have been individually extracted were between 30% and 65% and good reproducibility with relative standard deviation between 1% and 6% were obtained. All the test compounds were extracted simultaneously, the average recoveries were between 7% and 72% and low relative standard deviation with R.S.D. between 4% and 10% were achieved. Overall, for both extractions, higher recoveries were obtained from the compounds of lower polarity which are nitrobenzene and benzaldehyde compared to the more polar compounds, 2-chlorophenol and *p*-cresol. This was attributed to the non-polar and hydrophobic nature of the PS-DVB that favours the non-polar interaction between the less polar analytes and the adsorbent.

For the PS-DVB heptadecyl ketone adsorbent, high recoveries between 63% and 83% as well as good reproducibility with relative standard deviation between 2% and 7% were obtained (except for *p*-cresol that gave a recovery of 46.68%). This was probably due to the channelling of analytes when the test compounds were individually extracted. When the entire test compounds were extracted simultaneously, the average recoveries obtained were between 35% and 80% and low relative standard deviation between 2% and 5% were achieved. In the individual extraction, the less polar compounds exhibit lower recoveries compared to the more polar compounds while in the mixture extraction, highest recoveries were obtained for the compounds of lower polarity compared to the more polar compounds. Thus, it can be concluded that for this adsorbent, the less polar analytes will be extracted through interactions with the hydrophobic part of the polymer, while more polar analytes will be retained by the carbonyl groups. Subsequently, PS-DVB heptadecyl ketone is a suitable adsorbent used in solid phase extraction for all types of organic compounds in a wide polarity range.



The best recoveries were achieved with C<sub>18</sub>-silica while the recoveries obtained from synthesized PS-DVB and PS-DVB heptadecyl ketone were lower, which was attributed from the elution solvent that was used. Methanol is a better elution solvent for the extraction of polar compounds with C<sub>18</sub>-silica adsorbents due to its polarity and enables the dissolution of analytes retained in the C<sub>18</sub>-silica adsorbent, but is a weak elution solvent for PS-DVB adsorbent because the hydroxyl group gives poor surface contact with the polymer. However, PS-DVB heptadecyl ketone has significantly higher recoveries compare to PS-DVB because the presence of the carbonyl groups on its surface allowed better contact with the methanol. The incorporation of stearyl groups on PS-DVB improved the efficiency of the adsorbent by increasing polar interactions with the polar analytes. Higher surface area of the PS-DVB heptadecyl ketone allowed more interactions with the solutes and yielded higher retention of analytes. The stearyl group hydrophilicity increased the PS-DVB heptadecyl ketone's surface polarity and enabled the aqueous sample to have better contact with the resin surface and enhancing the mass transfer of analytes to the sorbents thus produce higher recoveries.

Based on this study, modified PS-DVB obtained by using stearyl chloride was better than using chloromethyl-styrene and linkage ether. The result indicated that PS-DVB heptadecyl ketone adsorbent has higher breakthrough volume either using nitrobenzene or 2-chlorophenol as the analytes at 30.60 mL and 20.7 mL, respectively, with its % R.S.D. was 11.56% and 7.59% compared to other modified PS-DVB or unmodified PS-DVB. Breakthrough volume for chloromethyl PS-DVB using nitrobenzene and 2-chlorophenol as the analytes were 1.23 mL and 2.07 mL, respectively. The breakthrough volumes for octadecoxy methyl PS-DVB were 1.03 mL (nitrobenzene) and 1.00 mL (2-chlorophenol).

Based on the results, PS-DVB heptadecyl ketone was found to be a better adsorbent compared to other modified and unmodified PS-DVB. But in this study, the chloromethyl PS-DVB and the octadecoxy methyl PS-DVB had not been successfully modified and consequently, their breakthrough volume and percentage recovery were lower compared to unmodified PS-DVB.

## 6.2 Suggestions

Through this study, several important aspects are recommended for future study in order to gain better performance to modify PS-DVB resins.

The characteristics of PS-DVB beads obtained were different compared to those of commercial PS-DVB. The average particle size of commercial PS-DVB beads was small and their shapes were spherical, whereas the average particle size of the home-made PS-DVB was larger. The home-made PS-DVB particles obtained were also spherical in shape. In order to get better results in the future, we are on the lookout for more regular particle size, and homogeneous surface morphology. We are looking forward to establish the effect of temperature, amount of DVB, and the design of stirrer. In this study, the concentration of DVB was 8% by weight. Generally, the percentage of smaller pores increases with larger amounts of DVB, which 10-20% by weight will likely to give the better results than the previous work. Higher polymerization temperature results in smaller pores. In this study, the polymerization temperature was at 70°C. It is expected that the use of higher temperatures will result in smaller pores and smaller particles.

The steps of modified PS-DVB in this study involved three steps, namely:

- Friedel Crafts acylation
- Chloromethylation of PS-DVB
- Williamson ether reaction

The resulting modified PS-DVB showed a disadvantage where the breakthrough volumes for the chloromethyl PS-DVB (chloromethylation of PS-DVB) and octadecyloxy methyl PS-DVB were lower compared to unmodified PS-DVB. To solve this problem, chloromethyl PS-DVB can be prepared by using chloromethyl methyl ether to produce better adsorbents, and also could be used for non-polar analytes.

In this work, using tubes or cartridges performed SPE. Hence, a bed height of more than 1 cm is usually used to ensure good retention of the desired sample compounds. However, this necessitates a relatively large volume of solvent to elute the adsorbed compounds. Further studies could be conducted by packing a tube with

disks 5-7 mm in diameter, cut from resin-loaded membranes. It would be possible to obtain efficient extraction with very short height of resin membrane. The reason for this is that the resin particles are closely packed, and evenly dispersed throughout the membrane. Since the particles are immobilized, it should be possible to avoid the channelling that would be likely in a tube containing only short height of a loose resin bed [48].

SPE with chemically modified sorbents has been carried out in the off-line and on-line modes by León-González and Pérez-Arribas [3]. In this work, SPE was carried out in the off-line mode. So further studies could be conducted to carry out SPE with unmodified PS-DVB or modified PS-DVB sorbents in the on-line mode. On-line procedures use an extraction sorbent in a pre-column. The methods, which combine SPE with HPLC, are the most frequently used, mainly to determine polar compounds in water. In the on-line procedures, there is no sample manipulation between preconcentration and analysis, so loss and contamination risks are avoided. Further more, detection limits and reproducibility values can be better. The off-line SPE can solve this problem too by looking for others method to fit in with our conditions. In this study, the analytes used were nitrobenzene and 2-chlorophenol in 20 ppm, perhaps the concentration of the analytes can be reduced lower than 20 ppm, or by looking for other analytes, which are more polar to suit the adsorbents.

As discussed previously [8, 40, 47, 13], ethyl acetate, acetonitrile and tetrahydrofuran are highly recommended and reported to be the suitable elution solvents for PS-DVB and modified PS-DVB as compared to methanol. Methanol is a weak elution solvent for PS-DVB adsorbent because present of the hydroxyl group on methanol makes it less solvate on the surface of the polymer. In this experiment, methanol was used as the elution solvent that resulted in lower recoveries for both PS-DVB and modified PS-DVB adsorbents. So, using ethyl acetate or acetonitrile as the elution solvent for PS-DVB and modified PS-DVB sorbents can carry out further studies. Higher breakthrough volume for modified PS-DVB or PS-DVB polymeric resins are well expected by using the recommended elution solvents.

## REFERENCES

1. Coutinho, F.M.B., Barbosa, C.C.R., and Rezende, S.M. Copolymers Based on Styrene and Divinylbenzene Synthesized in the Presence of PE HPA (Polyethylene Hydroxy Propyl Acrylate) Structural Characterization. *J. Europe. Polym.*, 1990. 31:1243-1250.
2. Iayedene, F., Guettaf, H., Bencheikh, Z., Saggou, A., and Rabia, I. 2-Ethyl - Hexanol and *n*-Heptane Diluents Mixture Effect on Textural Characteristic of Porous Styrene-Divinylbenzene Copolymer Beads. *J. Europe. Polym.*, 1996. 32:1091-1092.
3. Leon-Gonzalez, M.E., Perez-Arribas, L.V. Chemically Modified Polymeric Sorbents for Sample Preconcentrations. *J. Chromatogr. A*, 2000. 902:3-16.
4. Cantwell, F.F., Li, J. Influence of Solvent Uptake and Swelling by Poly (Styrene-Divinylbenzene) Column Packing on Sample Sorption Rate and Band Broadening in Reversed Phase Liquid Chromatography. *J. Chromatogr. A*, 1999. 835:3-18.
5. Masque, N., Galia, M., Marce, R.M., Borrull, F. Chemically Modified Polymeric Resin Used as Sorbent in a Solid-Phase Extraction Process to Determine Phenolic Compounds in Water: *J. Chromatogr. A*, 1997. 771:55-61.
6. Rogers V., Smith P.W.G. *Text Book of Practical Organic Chemistry*. 4<sup>th</sup> ed. New York: Longman London. 1978.

7. Bethmont, V., Fache, F., and Lemuire, M. Alternative Method to Williamson's Synthesis of Ethers. *Tetrahedron Letters*, 1995. 36:4235-4236.
8. Galceran, M.T., Jouregui, O. Determination of Phenols in Sea Water by Liquid Chromatography with Electrochemical Detection after Enrichment by Using Solid-Phase Extraction Cartridges and Disks. *Analytica Chimica. Acta*, 1995. 304:75-84.
9. Gelencser A., Kiss G., Krivacsy Z., Puchony Z.V., and Hlavay J. A simple Method for the Determination of Capacity Factor on Solid Phase Extraction Cartridges. I. *J. Chromatogr. A*, 1995. 693:217-225.
10. Bert Ooms, J.A., Marvan Gills, G.J., Duinkerken, A.R., Halmingh, O. Development and Validation of Protocols for Solid-Phase Extraction Coupled to IC and IC-MS. 2000: 52-57.
11. Abrams I.M., Millar J.R. A History of the Origin and Development of Macroporous Ion-Exchange Resins. *J. Reactive & Functional Polymers*, 1997. 35:7-22.
12. Chen, I., Feldman, H., Augenblick J. and Bread Danah. The Development and Analysis of Water-Repellent Polystyrene Derivatives. *J. The PGSS*, 1992. 177-200.
13. Jonsson S., Boren, H. Analysis Mono and Diesters of *o*-Pthalic Acid by Solid Phase Extraction with Polystyrene-Divinylbenzene Based Polymers. *J. Chromatogr. A*, 2002. 963:399-400.
14. Balakrishnan, T., Ford W. Particle Size Control in Suspension Copolymerization of Styrene, Chloromethylstyrene and Divinylbenzene. *J. Appl. Polym. Sci.*, 1982. 27:133-138.

15. Claudio L., and Monica, R.M.P. Synthesis of Cross-Linked Resin Based on Methacrylamide, Styrene and Divinylbenzene Obtained from Polymerization in Aqueous Suspension. *J. Europe. Polym.*, 2003. 39:291-296.
16. Klampf C.W., and Spanos, E. Separation of Priority Pollutant Phenols on Chemically Modified Poly (Styrene-Divinylbenzene) Resins by High Performance Liquid Chromatography. *J. Chromatogr. A*, 1995. 715:213-218.
17. Diana L.A., James, S.F., Michael, R., Buchemeiser, Norbert, A., and Gaunther, K.B. New High-Capacity Carboxylic Acid Functionalized Resins for Solid Phase Extraction of a Broad Range of Organic Compounds. *J. Chromatogr. A*, 1997. 786:259-268.
18. Yang, Y.B., Harrison, K., and Kindsvater, J. Characterization of a Novel Stationary Phase Derived from a Hydrophilic Polystyrene Based on Resin for Protein Cation-Exchange High Performance Liquid Chromatography. *J. Chromatogr. A*, 1996. 723:1-10.
19. Allcock, H.R. and Lampe, F.W. *Contemporary Polymer Chemistry*. 2<sup>nd</sup> ed. Englewood Cliffs, New Jersey: Prentice-Hall. 1990; 5, 47, 50-51, 58, 60, 153
20. Carraher, C.E. and Dekker, M.Jr. *Polymer Chemistry*. 6<sup>th</sup> ed. Florida, USA: Inc. 2003; 194-195, 299-300, 301-302, 310-311
21. Billmeyer, W.F. *Text Book of Polymer Science*. 3<sup>rd</sup> ed. London: John Willey & Sons. 1984.
22. Odion, G. *Principles of Polymerization*. New York: McGraw-Hill Book Company. 1970; 18-19, 270
23. Nail Handerson, J. (Ed.). Polymerization reactors and process: Goodyear Tire Rubber Company: *American Chemical Society symposium 104*, Washington, D.C. 1979.

24. Arshady, R. Guyot, A. Lin, J. Priddy, D.B. Rusanov, A.L. Sherington, D.C. Tauer, K. *Polymer Synthesis*. New York: Springer-Verlag. 1994.
25. Frantisek K. Homogeneous and Heterogeneous Sulfonation of Polymers. *Rev. Polym. Eng. Sci.*, 1998. 38:783-792.
26. Arshady, R. Beaded polymer supports and gels II. Physico-Chemical Criteria and Functionalization. *J. Chromatogr. A*, 1991. 586:199-219.
27. Buchmeiser, M.R. New Synthetic Ways for the Preparation of High Performance Liquid Chromatography Supports. *J. Chromatogr. A*, 2001. 918: 233-266.
28. Leofanti, G., Padovan, M., and Tozzola, G. Surface Area and Pore Texture of Catalysts. *Catalysts Today*, 1998. 41:207-219.
29. Munir Ahmed, Mohd.Airf Malik, Shahid Pervez, and Mohd.Raffiq. Effect of Porosity on Sulfonation of Macroporous Styrene-divinylbenzene Beads. *J. Europe Polym.*, 2004. 40:1609-1613.
30. Nash, D.C., Greath, G., E., and Howard, A.C. Modification of Polystyrenic Matrices for the Purification of Proteins Effect of the Adsorption of Poly (Vinyl Alcohol) on the Characteristics of Polystyrene-Divinylbenzene Beads for Use in Affinity Chromatography. *J. Chromatogr. A*, 1997. 758:53-64.
31. Xu, H. and Xizhang H. Preparation of Anion Exchangers by Reductive Amination of Acetylated Cross-Linked Polystyrene. *Reactive and Functional Polymer*, 1999. 42:235-242.
32. Chambers, T.K. and Fritz, J.S. Effect of Polystyrene-Divinylbenzene Resin Sulfonation on Solute Retention in High Performance Liquid Chromatography. *J. Chromatogr. A*, 1997. 797:139-147

33. Rabia, I., Zerouk, J., Kerkouche, M.K., and Belkhodja, M. Chemically and Textural Characteristics of Porous Styrene-Divinylbenzene Copolymers as a Function of Chlorosulfonation Reaction Parameters. *Reactive and Functional Polymers*, 1996. 28:279-28
34. Poinescu, Ig.C. Camelia, B., and Christina, V. Styrene-Divinylbenzene Copolymers: Influence of the Diluents on Network Porosity. *J. Appl. Polym. Sci.*, 1984. 29:23-34.
35. Bacquet, M., Salunkhe, M., and Caze, C. Influence of Chlorosulfonation on Textural Chemical Parameters of Styrene-Divinylbenzene Porous Copolymers. *Reactive Polymer*, 1992. 16:61-69
36. Biermann, U. Lutzen, A. Marcel, S.F. and Metzger, J.O. Regioselective Cationic1,2-and1,4-additions Forming Carbon-Carbon Bond to Methyl Santalbate a Conjugated Enzyme. *J. Org. Chem. Europe.*, 2000: 3069-3073.
37. Bacquet, M., and, Caze, C. Spatial Distribution of Pendent Vinyl Groups During Chloromethylation of Macroporous Styrene-Divinylbenzene Copolymers. *Reactive Polymers*, 1988. 9:147-153.
38. Theodoropoulos, G. Bouranis, D.L. and Valkanas, G.N. Efficient"One-Pot" Synthesis of Suspension Crosslinked Sulfonated Polystyrene Via a Friedel-Crafts Reaction. *J. Appl. Polym. Sci.*, 1992. 46:1461-1465.
39. Dumont, P.J., and Fritz, J.S. Effect of Resin Sulfonation on the Retention of Polar Organic Compounds in Solid-Phase Extraction. *J. Chromatogr. A*, 1995. 691:123-131.
40. Salawati Subuh, Mohd.Marsin Sanagi, Ahmedy Abu Naim, and Asiah Hussain. *Pembangunan danPenggunaan Bahan Penjerap dan Fasa Pegun dalam Analisis Kimia*. Laporan Akhir Penyelidikan IRPA Vot 72298, University Teknologi Malaysia; 2002.



41. Mahdavian A.R., and Khoee S. A facile and Efficient Method for Preparation of Chiral Supported Poly (Styrene-Divinylbenzene) Copolymers. *Reactive and Functional Polymer*, 2002. 50:217-223.
42. Dominic, C.N, and Howard, A. Modification of Polystyrenic Matrices for the Purification of Proteins. II: Effect of the Degree of Glutaraldehyde-Poly (Vinyl Alcohol) Crosslinking on Various Dyes Ligand Chromatography Systems: *J. Chromatogr. A*, 1997. 776:55-63.
43. Masque, N., and Galia, M. New Chemically Modified Polymeric Resin for Solid Phase Extraction of Pesticides and Phenolic Compounds from Water: *J. Chromatogr. A*, 1998. 803:147-155.
44. Powell, M.W. Development of a Binary Solid-Phase Extraction Cartridge Use in Screening Water Sample for Organic Pollutants. *J. Chromatogr. A*, 1995. 697:101-105.
45. Schmidt, L., and Fritz, J.S. Ion-Exchange Preconcentration and Group Separation of Ionic and Neutral Organic Compounds. *J. Chromatogr. A*, 1993. 640:145.
46. Smigol, V., and Svec, F. Synthesis and Properties of Uniform Beads Based on Macroporous Copolymer Glycidyl Methacrylate-Ethylene Dimethacrylate: A way to Improve Separation Media for HPLC. *Journal of Appl. Polym. Sci.*, 1992. 46:1439.
47. Sun, J.J., and Fritz, J.S. Chemically Modified Resins for Solid Phase Extraction. *J. Chromatogr. A*, 1992. 590:197-202.
48. Schmidt, L., Sun, J.J., Hagen, D.F., Markelle, C.G., and Wisted, E.E. Solid-Phase Extraction of Phenols Using Membranes Loaded with Modified Polymeric Resins. *J. Chromatogr. A*, 1993. 641:57-61.

49. Dai J., Yang X., and Carr P.W. Comparison of the Chromatography of Octadecyl Silane Bonded Silica and Polybutadiene-Coated Zirconia Phases Based on A Diverse Set of Cationic Drugs. *J. Chromatogr. A*, 2003. 1005:63-82.
50. Camel,V. Solid-Phase Extraction of Trace Elements. *Spectrochimica Acta B*, 2003. 58:1177-1233.
51. Yu, J.C., Jiang, Z.T., Liu, H.Y., Yu, J. and Zhang, L.  $\beta$ -Cyclodextrin Epichlorohydrin Copolymer as A Solid-Phase Extraction Adsorbent for Aromatic Compounds in Water Samples. *Anal. Chim. Acta*, 2003. 477:93-101.
52. Lindström, A., Albertsson, A. and Hakkarainen, M. Development of a Solid Phase Extraction Method for Simultaneously Extraction of Adipic Acid, Succinic Acid and 1,4-butanediol Formed During Hydrolysis of Poly(butylenes adipate) and Poly(butylenes succinate). *J. Chromatogr. A*, 2004. 1022:171-177.
53. Melo, L.F.C., Collins, C.H. and Jardim, C.S.F. New Materials for Solid-Phase Extraction and Multiclass High-Performance Liquid Chromatography Analysis of Pesticides in Grapes: *J. Chromatogr. A*, 2004. 1032:51-58
54. Mayer, D.L., and Fritz, J.S. Silicate as a Sorbent for Solid Phase Extraction. *J. Chromatogr. A*, 1997. 771:45-53.
55. Fritz, J.S., and Masso, J. J. Miniaturized Solid-Phase Extraction with Resin Disks. *J. Chromatogr. A*, 2001. 909:79-85.
56. Fritz, J.S., Dumont, P.J., and Schmidt, L.W. Methods and Materials for Solid-Phase Extraction. *J. Chromatogr. A*, 1995. 691:133-140.
57. Mohd. Marsin Sanagi. *Teknik Pemisahan dalam Analisis Kimia*. Universiti Teknologi Malaysia, Skudai, Johor Darul Ta'zim.1998.

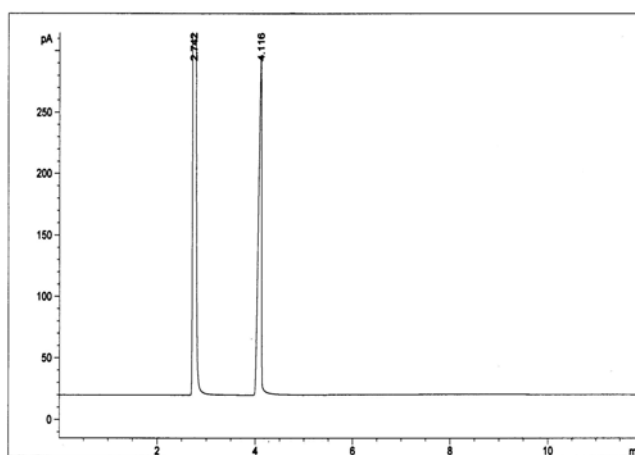
58. Aspinall, H.C. Greeves, N. Man Lee, W., McIver, E.G., and Smith, P.M. An Improved Williamson Etherification of Hindered Alcohols promoted by 15-Crown-5 and Sodium Hydride. *Tetrahedron Letters*, 1997. 38: 4679-4682.
59. Grob, R.L. *Modern Practice of Gas Chromatography*. 2<sup>nd</sup> ed. New York: John Wiley & Sons. 1985; 1-3, 214, 240.
60. Tham Ee Mun, *Chemical Characterization and Application of Poly (Styrene-Divinylbenzene) and C<sub>18</sub> Modified PS-DVB Adsorbent: Solid Phase Extraction (SPE) of Test Compounds*. Tesis Ijazah Sarjana Muda Sains. Universiti Teknologi Malaysia; 2004.
61. Cai, Y.Q., Jiang, G.B., Liu, J.F. and Zhou, Q.X. Multi-Walled Carbon Nano Tubes Packed Cartridge for the Solid Phase Extraction of Several Phthalates Esters from Water Samples and Their Determination by High Performance Liquid Chromatography. *Anal. Chim. Acta*, 2003. 494:149-156.
62. Ersöz, A., Say, R. and Denizli, A. Ni (II) Ion-Imprinted Solid Phase Extraction and Preconcentration in Aqueous Solutions by Packed-bed Columns. *Anal. Chim. Acta*, 2004. 502:91-97.
63. Bagheri, H. and Mohammadi, A. Pyrrole-based Conductive Polymer as the Solid-Phase Extraction Medium for the Preconcentration of Environmental Pollutants in Water Samples Followed by Gas Chromatography with Flame Ionization and Mass Spectrometry Detection. *J. Chromatogr. A*, 2003. 1015: 23-30.
64. Yi, L. and Pietrzyk, D.J. Capillary-electrochromatographic Separations with Copolymeric Reversed Stationary Phase and Ion Exchanger Packed Columns. *J. Chromatogr. A*, 2001. 920:367-375.

65. Weigel, S., Kallenborn, R. and Hühnerfuss, H. Simultaneous Solid-phase Extraction of Acidic, Neutral and Basic Pharmaceuticals from Aqueous Samples at Ambient (Neutral) pH and Their Determination by Gas Chromatography-Mass Spectrometry. *J. Chromatogr. A*, 2004. 1023:183-195.
66. Fontanals, N., Galià, M., Marcé, R.M. and Borrull, F. Solid Phase Extraction of Polar Compounds with a Hydrophilic Copolymeric Sorbent. *J. Chromatogr. A*, 2004. 1030:63-68.
67. Klingenberg, A. and Seubert, A. Sulfoacylated Poly (Styrene-Divinylbenzene) Copolymers as Resins for Cation Chromatography. Comparison with Sulfonated, Dynamically Coated and Silica Gel Cation Exchangers. *J. Chromatogr. A*, 2002. 946: 91-97.
68. Sychoy, C.S., Ilyin, M.M., Davankov, V.A. and Sochilina, K.O. Elucidation of Retention Mechanisms on Hyper Cross-Linked Polystyrene Used as Column Packing Material for High-Performance Liquid, Chromatography. *J. Chromatogr. A*, 2004. 1030:17-24.

## APPENDICES

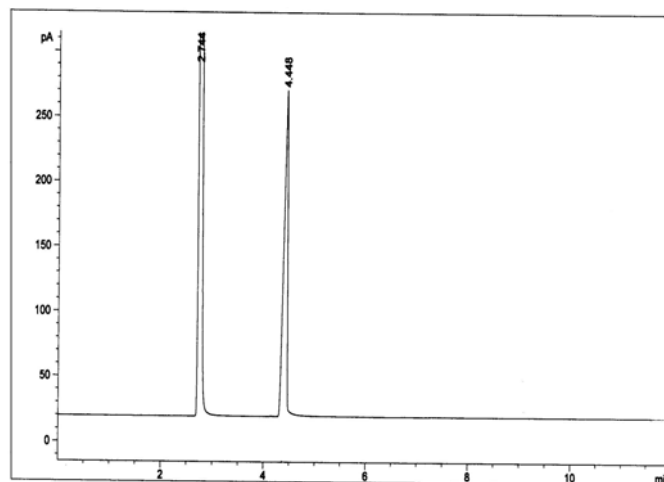
### APPENDIX A1

Example of chromatogram for Benzaldehyde stock solution (100,000 ppm) for the determination of retention time and response factor with Ultra-1 column (30 m  $\times$  250  $\mu$ m  $\times$  0.20  $\mu$ m)



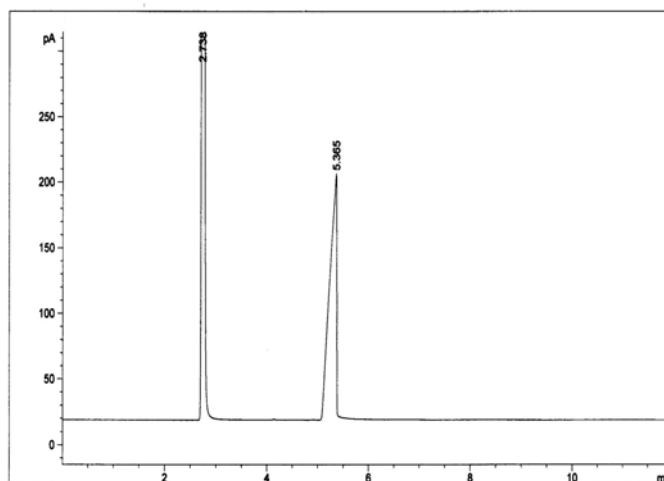
### APPENDIX A2

Example of chromatogram for 2-Chlorophenol stock solution (100 000 ppm) for the determination of retention time and response factor with Ultra-1 column (30 m  $\times$  250  $\mu$ m  $\times$  0.20  $\mu$ m)



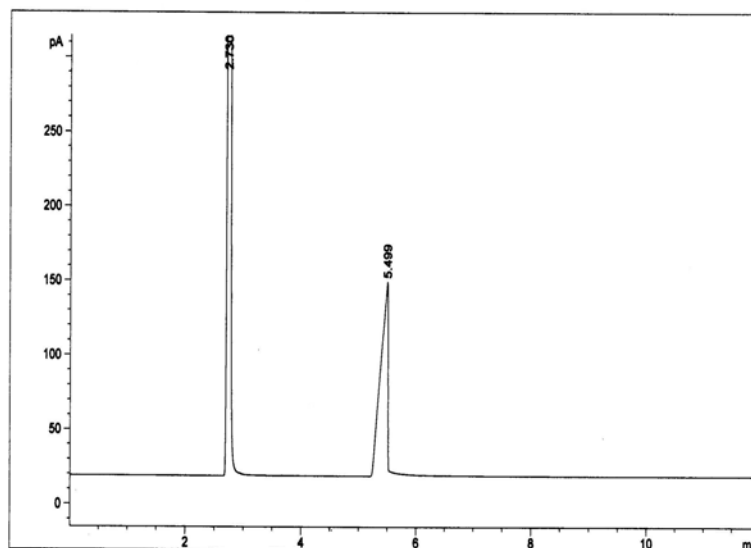
### APPENDIX A3

Example of chromatogram for *p*-Cresol stock solution (100,000 ppm) for the determination of retention time and response factor with Ultra-1 column (30 m  $\times$  250  $\mu$ m  $\times$  0.20  $\mu$ m)



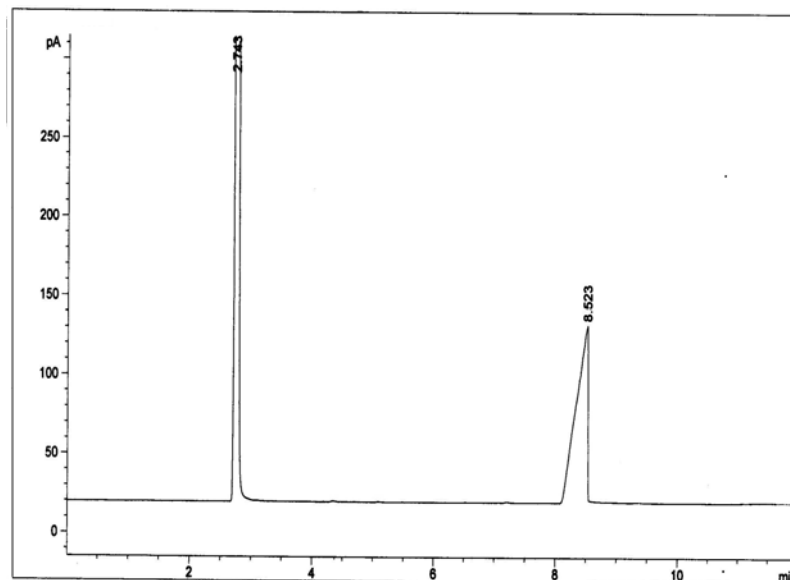
### APPENDIX A4

Example of chromatogram for Nitrobenzene stock solution (100 000 ppm) for the determination of retention time and response factor with Ultra-1 column (30 m  $\times$  250  $\mu$ m  $\times$  0.20  $\mu$ m)



**APPENDIX A5**

Example of chromatogram for butyrophenone stock solution (100 000 ppm) for the determination of retention time and response factor with Ultra-1 column (30 m  $\times$  250  $\mu$ m  $\times$  0.20  $\mu$ m)



## APPENDIX B 1

### Calculation of Concentration of Analytes

From the results of concentration obtained, the recovery values for each test compound can be determined by using equation 3.3, and equation 3.4 given in Section 3.8, and Section 3.9.

$$\begin{aligned} \text{Benzaldehyde's concentration, } M_x &= \frac{F_s}{F_x} \times \frac{\text{Average } A_x}{\text{Average } A_s} \times \text{Butyrophenone's concentration, } M_s \\ &= 1715 \text{ ppm} \end{aligned}$$

## APPENDIX B2

### Calculation of Percentages of Recovery

$$\% \text{ Recovery} = \frac{\text{Average } M_x}{\text{Sample's concentration before extraction}} \times 100\% \times \text{Dilution Factor}$$

$$\% \text{ Recovery} = \frac{1715 \text{ ppm}}{100,000 \text{ ppm}} \times 100\% \times 50$$

$$= 85.77 \%$$



**APPENDIX B3****Calculation of Breakthrough Volume**

Where the data:

- The chart speed = 0.5 cm/min
- Flow rate = 1.0 mL/min
- Retention distance = 7.20 cm

Based on the equation in 3.1 and 3.2, in Section 3.5.3.

$$\text{Retention time} = 7.20 \text{ cm} / 0.50 \text{ cm/min}$$

$$\text{Retention time} = 14.40 \text{ min}$$

$$\text{The breakthrough volume} = 14.40 \text{ min} \times 1.0 \text{ mL/min}$$

$$\text{The breakthrough volume} = 14.40 \text{ mL}$$

**APPENDIX C1****The Effect of Reaction Time on Porosity and Particle Size of Home-made PS-DVB**

<b>Reaction time (h)</b>	<b>Particle size (<math>\mu\text{m}</math>)</b>	<b>Average pore width (<math>\text{\AA}</math>)</b>	<b>Total pore volume <math>\text{cm}^3/\text{g}</math></b>
1	117	35	0.001837
5	110	76	0.001840
10	108	164	0.002666
15	106	300	0.008056
20	93	65	0.001258

**APPENDIX C2****The Effect of Reaction Time on the Yield of Home-made PS-DVB**

<b>Reaction time (h)</b>	<b>Yield (g)</b>
1	13.50
5	61.88
10	123.76
15	124.00
20	126.62

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Stationary Phases**

**Volume 2**

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NORSYARIZA ABD AZIZ**

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## UNIVERSITI TEKNOLOGI MALAYSIA

BORANG PENGESAHAN  
LAPORAN AKHIR PENYELIDIKAN

TAJUK PROJEK: DEVELOPMENT AND APPLICATION OF NEW MODIFIED  
POLY(STYRENE-DIVINYLBENZENE) ADSORBENTS AND  
CHROMATOGRAPHY STATIONARY PHASES. VOLUME 2:  
p-ETHANOYL-PS-DVB, p-2-PROPANOYL-PS-DVB, AND  
ZICONIA-MODIFIED PS-DVB

Saya MOHD MARSIN BIN SANAGI  
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## ABSTRACT

Poly(styrene-divinyl benzene) (PS-DVB) resin is an attractive adsorbent for extraction and separation of various types of compounds due to its stability over the pH range of 1-14. However, PS-DVB resin is known to have hydrophobic surfaces that highly retain non-polar compounds while poorly retain polar compounds. To improve its use in the separation or extraction of polar compounds, PS-DVB resin must be chemically or physically bonded to hydrophilic groups to reduce its hydrophobic surface. The objectives of this project were to modify PS-DVB phases by introducing moieties that can increase the dispersive forces and lower the hydrophobicity of the PS-DVB phases and to examine the characteristics and applications of the modified PS-DVB adsorbents.

The PS-DVB adsorbents were prepared by suspension polymerization method with polyvinyl alcohol as the suspension stabilizer at a stirring speed of 1000 rpm for 20 h. The second approach (Volume 2) explores the development of PS-DVB resins modified with acetyl chloride, chloroacetone and zirconyl chloride. Modifications of the PS-DVB adsorbents were carried out via Friedel-Crafts acylation reaction with acetyl chloride and chloroacetone using Lewis acid catalyst, Grignard reaction of the product with methyl magnesium chloride and reaction of the product with zirconium(IV) oxide chloride octahydrate. The products obtained were characterized using infrared spectroscopy, scanning electron microscopy, nitrogen adsorption analysis and thermal gravimetric analysis. The performance of the PS-DVB-based phases was evaluated by investigating its adsorption-desorption efficiency in solid phase extraction. Comparative recovery studies showed that the *p*-ethanoyl-PS-DVB and *p*-2-propanoyl-PS-DVB resins were superior compared to unmodified PS-DVB and zirconia-modified PS-DVB for solid phase extraction of the test compounds 2-chlorophenol, nitrobenzene and propiophenone.

## ABSTRAK

Resin poli(stirena-divinil benzena) (PS-DVB) merupakan penjerap yang menarik untuk pengekstrakan dan pemisahan pelbagai jenis sebatian disebabkan kestabilannya pada julat pH 1-14. Walau bagaimanapun, resin PS-DVB diketahui mempunyai permukaan yang hidrofobik yang sangat menahan sebatian tak berkutub manakala tidak menahan sebatian berkutub. Untuk memperbaiki penggunaan bahannya dalam pemisahan atau pengekstrakan sebatian berkutub, resin PS-DVB mesti diikat secara kimia atau fizik kepada kumpulan hidrofilik untuk mengurangkan kehidrofobikan permukaannya. Objektif projek ini ialah untuk mengubahsuai fasa PS-DVB dengan memasukkan moiety yang boleh meningkatkan daya serakan dan mengurangkan kehidrofobikan fasa tersebut dan untuk mengkaji ciri-ciri dan penggunaan PS-DVB terubahsuai itu.

Penjerap PS-DVB telah disediakan dengan kaedah pembolimeran ampaiian dengan alkohol polyvinil sebagai penstabil ampaiian pada kelajuan putaran 1000 rpm selama 20 jam. Pendekatan yang kedua (Jilid 2) mengkaji pembangunan PS-DVB terubahsuai dengan asetil klorida, kloroaseton dan zirkonil klorida telah dibangunkan. Pengubahsuaian terhadap penjerap PS-DVB telah dijalankan melalui tindak balas pengakilan Friedel Crafts dengan asetil klorida dan kloroaseton menggunakan mangkin asid Lewis, tindak balas Grignard hasilnya dengan metil magnesium klorida dan tindak balas hasilnya dengan zirkonia(IV) oksida oktahidrat. Bahan penjerap yang dihasilkan dicirikan dengan menggunakan spektroskopi infra merah, mikroskopi imbasan elektron, analisis penjerapan nitrogen dan analisis gravimetri termal. Prestasi bagi fasa pegun berasaskan PS-DVB itu telah dinilai dalam kajian penjerapan-penyahjerapan melalui teknik pengekstrakan fasa pepejal. Perbandingan nilai perolehan semula analit menggunakan metanol sebagai pengelusi menunjukkan bahawa etanoil-PS-DVB dan 2-pentanoil-PS-DVB memberikan nilai perolehan semula yang tinggi berbanding fasa pegun PS-DVB tulen dan PS-DVB terubahsuai zirkonia.



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## LIST OF SYMBOL

$A_s$	-	Internal standard peak area
$A_x$	-	Test compound peak area
BPO	-	Benzoyl Peroxide
DVB	-	Divinyl benzene
$F_s$	-	Internal standard response factor
FTIR	-	Fourier Transform Infrared
$F_x$	-	Test compound response factor
GC-FID	-	Gas Chromatography-Flame Ionization Detector
h	-	Hour
IS	-	Internal standard
KBr	-	Potassium bromide
$M_s$	-	Internal standard concentration (ppm)
$M_x$	-	Test compound concentration (ppm)
$P/P_o$		Relative pressure; obtained by forming the ratio of the equilibrium pressure and vapour pressure $P_o$ of the adsorbate at the temperature where the isotherm is measured
ppm	-	Parts per million
PS-DVB	-	Poly(styrene-divinyl benzene)
R.S.D.	-	Relative standard deviation
SPE	-	Solid Phase Extraction
$t_R$	-	Retention time
% R	-	Percentage of recovery
$\lambda$	-	Wavelength

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Adsorbents and Chromatography Stationary Phases**

The material on the surface of which adsorption takes place is called the adsorbent and the substance adsorbed is called the adsorbate (Gurdeep, 1974). The common surface separating the two phases, where the adsorbed molecules concentrate is referred to as the interface. The larger the surface area of the adsorbent, the more is the adsorption. Some examples of the adsorbents are charcoal, silica gel, metals, polymers and etc. The term adsorption appears to have been introduced by Kayser in 1881 to connote the condensation of gases on free surfaces, in contradistinction to gaseous absorption where the molecules of gas penetrate into the mass of the absorbing solid. Adsorption (strictly, physical adsorption) has now been internationally defined as the enrichment (i.e. positive adsorption or simply adsorption) or depletion (i.e. negative adsorption) of one or more components in an interfacial layer (Gregg and Sing, 1982).

The various forms of chromatography are classified according to the nature of the mobile and stationary phases. The mobile phase may be gaseous or liquid, while the stationary phase may be solid or liquid. For example, in gas liquid chromatography (GLC), the liquid stationary phase is dispersed on an inert solid

support. The liquid phase is held on the surface and in the pores of the support, while the mobile gas phase flows through the spaces between particles (Conder and Young, 1979).

The choice of adsorbents as the proper stationary phase is one of the most important decisions in column chromatography. The use of adsorbents of porous polymers and inorganic salt, either porous or non-porous and modified oxides, as well as surfaces of dense monomolecular polymer layers absorbed on the sufficiently developed and homogenous surface of non-porous and wide-porous adsorbent, opens extensive possibilities for selecting and controlling the nature of the adsorbent surfaces and, therefore, for controlling the selectivity of gas adsorption columns (Baiulescu and Ilie, 1975). In the last two decades, separation sciences have faced important developments. Starting with solid-phase extraction (SPE) in the 1980s, other new techniques, e.g., supercritical fluid extraction (SFE), supercritical fluid chromatography (SFC) and capillary electrochromatography (CEC) have been introduced (Liu and Pietrzyk, 2001). Besides these new analytical tools, “classical” separation techniques such as high performance liquid chromatography (HPLC) have been further developed and optimized. New inputs from synthetic chemistry and more efficient analytical tools for their characterization significantly enhanced the quality of liquid chromatography (LC) supports in terms of stability, reproducibility, selectivity and efficiency (Buchmeiser, 2001).

## **1.2 Research Background**

The preparation of alternative stationary phase supports in chromatographic science is an important area that aims to develop new support materials that offer novel selectivities or overcome the shortcomings of silica supports (Shalliker *et al.*, 1997). The ideal chromatography support particle should have a high surface area on which a wide variety of chemical moieties can be irreversibly and inalterably deposited to provide useful selectivity for a number of separation problems. It should

be physically and chemically stable over a wide range of pressure, pH, temperature and solvent conditions. It should be available in a variety of particle diameters as well as pore sizes and volumes (Nawrocki *et al.*, 1993).

Microparticulate, macroporous, poly(styrene-divinyl benzene) (PS-DVB) copolymeric reversed-phase adsorbent have been used very successfully as stationary phases in HPLC (Liu and Pietrzyk, 2001). Organic beaded polymer supports based on polystyrene are almost exclusively prepared by emulsion, suspension, dispersion and precipitation polymerization techniques (Buchmeiser, 2001). However, PS-DVB resins are known to have hydrophobic surfaces that highly retain non-polar compounds while poorly retain polar compounds.

Although silica and modified silicas are the most widely used and most useful chromatographic supports, it is well known that silica and bonded silicas are not stable outside the range of pH 2 to approximately 8 (Wehrli *et al.*, 1978). Above pH 8, silica is subjected to attack by alkali and it dissolves. Below approximately pH 2, the siloxane linkages which hold bonded phases to silica are subjected to hydrolytic attack and are slowly removed from the surface (Glajeh *et al.*, 1987). The dissolution of silica and removal of bonded phase is accelerated at high temperature and leads to changes in retention, selectivity and peak shape, loss of column bed integrity, and contamination of product in preparative chromatography. The typical commercial alkyl silane bonded silica phase is seldom used at more than 20-30°C higher than room temperature because of its instability at high temperature (McNeff *et al.*, 2000).

Another interesting development is in the synthesis and application of zirconia stationary phases. The surface area of zirconia is low when compared to the silica supports typically used as chromatographic supports. However, it is important to recognize when considering the surface area data that true density of monoclinic zirconia is approximately 5.8 g mL<sup>-1</sup> whereas the density of commercial silica is 2.3 g mL<sup>-1</sup>. Cubic zirconia is reported to have the highest density 6.27 g mL<sup>-1</sup> (Nawrocki *et al.*, 1993). Due to its higher density, the surface area of zirconia is comparable to that of silica in terms of surface area per unit volume.

### **1.3 Statement of Hypothesis**

PS-DVB resins have a hydrophobic surface. To extend its applicability in extraction or chromatographic performance, the PS-DVB resins should have a chemical bonding or hydrophilic groups to decrease and mask its hydrophobic surface. Chemical modification on the PS-DVB resins can be carried out by the Friedel Craft acylation reaction and Grignard reaction. Zirconia can be then introduced onto the PS-DVB resin. Zirconia-modified PS-DVB resin is expected to have lower hydrophobic surface and more stable compared with unmodified PS-DVB resin.

### **1.4 Research Aim**

The aim of this research is to synthesize new adsorbents based on PS-DVB resins and study the performance of the adsorbents by physiochemical methods.

### **1.5 Research Objectives**

- i. To synthesize PS-DVB adsorbent using the suspension polymerization method.
- ii. To modified PS-DVB adsorbents using three steps or reactions:
  - (a) Friedel Crafts acylation reaction of PS-DVB with acetyl chloride and chloroacetone using Lewis acid catalyst;
  - (b) Grignard reaction of the product (a) with methyl magnesium chloride;and

- (c) reaction of the product (b) with zirconium(IV) oxide chloride octahydrate.
- iii. To characterize and study the performance of the new adsorbents by physiochemical methods.

## **1.6 Scope of Research**

A complete reaction scheme is given in Figure 1.1. In this research, PS-DVB resins were synthesized using the suspension polymerization method. Optimization of the suspension polymerization method was carried out by studying the effect of reaction time, effect of stabilizer and effect of seeding polymerization. The physical properties of the PS-DVB resins were studied by fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetry analysis, and nitrogen adsorption analysis. Batch of PS-DVB resins which exhibit the most suitable adsorbent properties such as high surface area, minimum pore size was chosen to be modified. Comparison of the physical properties of both native and modified PS-DVB phases was carried out and the performance of the modified PS-DVB phases was evaluated by investigating its adsorption-desorption efficiency in solid phase extraction.



## a) Preparation of PS-DVB resin

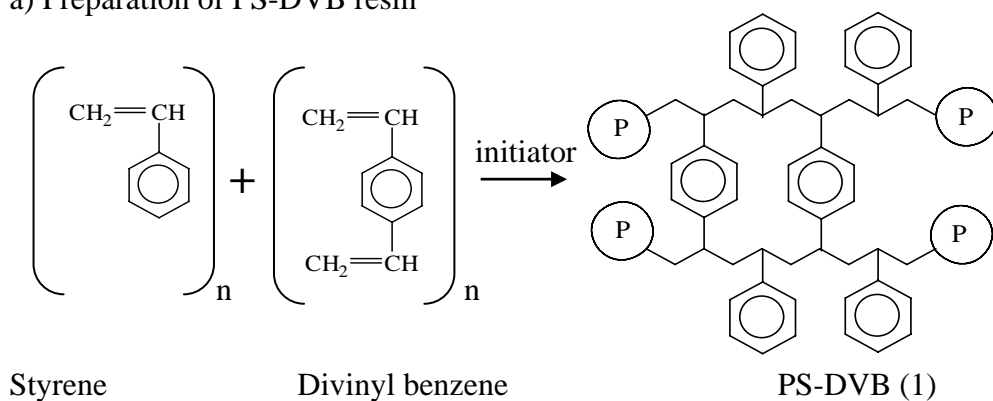
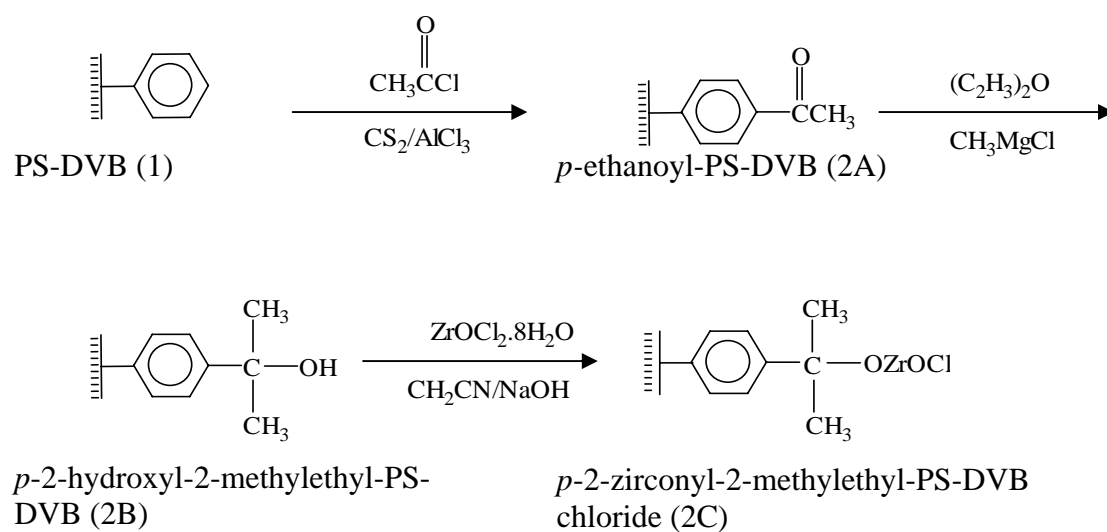
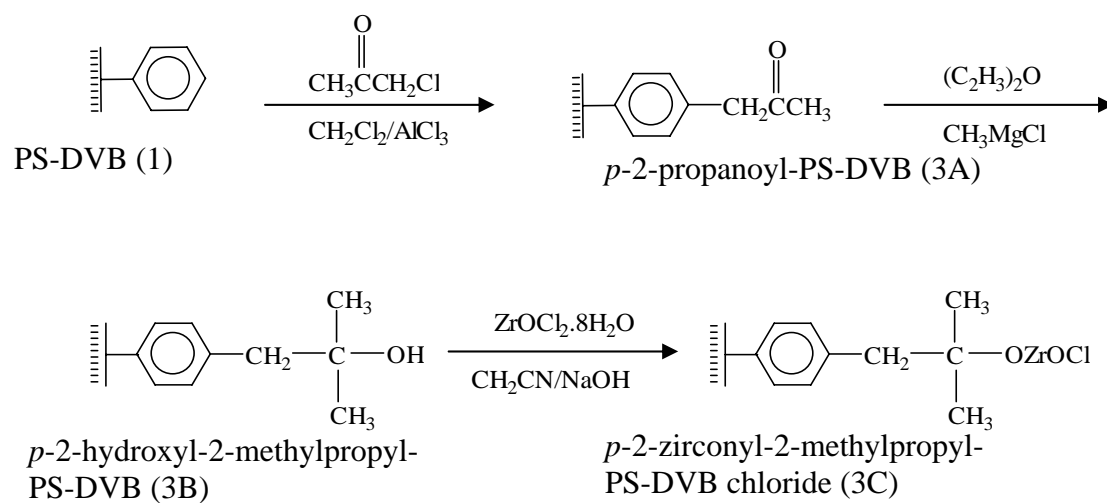
b) Preparation of *p*-2-zirconyl-2-methylethyl-PS-DVB chloride (2C)c) Preparation of *p*-2-zirconyl-2-methylpropyl-PS-DVB chloride

Figure 1.1 A complete reaction scheme

## **1.7 Outline of the Research Report**

This research report consists of six chapters. Chapter 1 presents general background of this research, research aim, research objectives and scope. Chapter 2 compiles the literature reviews and theoretical background on PS-DVB and Zirconia, modification of PS-DVB and its application as an adsorbent for solid phase extraction (SPE). The procedures for characterization and application of the synthesized materials are presented in Chapter 3. Chapter 4 reports the results and discusses the preparation of PS-DVB, and modification of PS-DVB. It also describes the characterization and application of unmodified and modified PS-DVB as adsorbents in the solid phase extraction analysis. The concluding Chapter 5 summarizes this research report by presenting the overall conclusions and suggestions for future study.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Poly(styrene-divinyl benzene)

PS-DVB resins are widely used as ion-exchangers (Coutinho *et al.*, 2004; Chambers and Fritz, 1998; Nash and Chase, 1998; Ohta *et al.*, 2004) polymeric absorbents (León-González and Pérez-Arribas, 2000), chromatographic separation media (Li *et al.*, 1997) and as solid supports for organic synthesis (Gauthier *et al.*, 2004). The PS-DVB resins with fixed pores can be obtained by suspension polymerization (Coutinho *et al.*, 2004; Maria *et al.*, 2003a and 2003b; Martin *et al.*, 2003), which is particularly suited to the production of large spherical beads typically in the range 5-1000  $\mu\text{m}$ . Porous copolymers from a number of related monomers have also been synthesized by the same technique, e.g., methacrylamide styrene-divinyl benzene, acrylonitrile-divinyl benzene, glycidyl methacrylate-ethyleneglycol dimethacrylate, methacrylic acid-triethyleneglycol dimethacrylate, acrylic acid-triethyleneglycol dimethacrylate, acrylamide-ethylene glycol dimethacrylate, 4-vinylpyridine-divinyl benzene, etc. (Malik *et al.*, 2004).

The PS-DVB resin is prepared by free radical cross-linking copolymerization of styrene and divinyl benzene monomers in the presence of diluent, which can be a solvent, a non-solvent or a linear polymer, and is the pore forming agent. In a

solvating diluent, macroporous polymers are only produced when the divinyl benzene concentration is high, and the monomer concentration is diluted. However, when non-solvating diluents are used, the macroporosity appears at lower concentrations of divinyl benzene and with less diluted monomers (Legido-Quigley and Smith, 2004a).

Two groups of PS-DVB resins are commonly described (Howdle *et al.*, 2000). The first, referred to as gel-type species, are lightly crosslinked, typically employing 0.5-2 mol % DVB, and rely upon solvation of individual polymer chains by a thermodynamically good solvent to swell the polymeric network and allow access to the support. In the swollen state, such resins are soft, compressible, and relatively fragile in shear. The second, referred to as macroporous species, are usually more highly crosslinked, and possess a complex system of permanent pores created by employing a porogen (usually inorganic solvent) in the polymerization. The pore system can be accessed by thermodynamically poor solvents as well as good ones, and these resins are more rigid even when in contact with solvent. They can therefore be employed in packed columns.

### **2.1.1 Advantages and Drawbacks of PS-DVB**

PS-DVB copolymers overcome many of the limitations of bonded silicas, especially those related to the limited pH stability or the presence of the silanol groups (Li *et al.*, 1996). The application of silica-based support is limited by the low stability of silica at alkaline pH values and by the unwanted interactions between polar solutes and remaining free silanol groups not covered by the hydrophobic ligand (Hosoya *et al.*, 1995). Porosity and mechanical stability can be altered by varying the cross-linking through the variation of the DVB content. PS-DVB is not soluble in water, inert and very hydrophobic. It is white in color and non-toxic, thus it does not biodegrade easily and does not have toxicity effect on marine life.

In the last decade, there has been a growing interest in polymeric materials for use in reversed-phase high-performance liquid chromatography (HPLC). In particular, resins based on PS-DVB are stable with eluents from pH 1-14 and give excellent separations. Some difficulties have been associated with polymeric resins, such as swelling in the presence of organic solvents. However, rapid improvements are being made in stability and performance so that polymeric resins can be considered to be very attractive for HPLC (Sun and Fritz, 1990).

Due to its hydrophobic nature, the synthetic polymer in certain cases can be used directly as a reversed-phase stationary phase, without the need for further derivatization. However, there are two commonly derivatization methods of introducing alkyl groups onto the surface of the synthetic polymer. Firstly, a monomer such as an alkyl styrene can be included in the polymerization mixture. However, it must be soluble in the porogen and precipitate when the polymer is formed. Secondly, the surface of the polymer can be alkylated after formation by using for example, a strong Friedel Crafts catalyst (alkyl halide in organic solvent) (Legido-Quigley *et al.*, 2004b).

In general, PS-DVB resins have greater analyte retention, mainly for polar compounds, than bonded silicas, because their hydrophobic surface contains a relatively large number of active aromatic sites that allow  $\pi$ - $\pi$  interactions (León-González and Pérez-Arribas, 2000). In comparison with silica sorbents, PS-DVB resin is more stable at acid-base pH concentration and according to Rodriguez *et al.* (2000) PS-DVB resin has higher capacity for polar analytes. This can be attributed to a much larger carbon content (nearly 90% as compared to the maximum 18% of C<sub>18</sub>-silica sorbents) but specially to the higher surface-area exhibited by polymers (many of commercial available ones have areas of  $>1000 \text{ m}^2\text{g}^{-1}$  as compared to 200-600  $\text{m}^2\text{g}^{-1}$  for C<sub>18</sub>-silica sorbents).

PS-DVB copolymers with partially substituted quaternary ammonium groups or slightly sulfonated have also been used for SPE of organic solutes, because they have excellent hydrophilicity, thus extracting polar organic compounds more efficiently than underivatized resins do (León-González and Pérez-Arribas 2000). In general, all these derivatized PS-DVB resins are not commercially available, except

those with sulfonic or quaternary ammonium groups, which are also ion exchangers. Therefore, when they are needed, they have to be prepared in the laboratory by modifying a commercially available resin.

Retention of polar phenols on PS-DVB sorbents can be improved by the introduction of polar groups into the polymer. Resulting materials still retain the high capacities to trap less polar phenols, but in addition, the hydrophilic character of the introduced functional group, improves their wetting characteristics and, consequently aids mass transfer of most polar phenols from the water solution to the sorbent. Most common groups used to modify polymeric sorbents are acetyl, hydroxymethyl, benzoyl, *o*-carboxybenzoyl, carboxylic and sulphonic acid. C<sub>18</sub>-silica sorbents have also been modified with quaternary ammonium salts (Rodriguez *et al.*, 2000).

### 2.1.2 Chemical Modification of PS-DVB Resin

In last 20 years, the performance and suitability for solid phase extraction (SPE) of several polar functional groups modifying PS-DVB have been studied. These groups are listed in Table 2.1. They are mainly acyl derivatives which sometimes have one or more carboxylic acid groups (León-González and Pérez-Arribas, 2000).

Sun and Fritz (1990 and 1992), modified PS-DVB with alcohol and acetyl functional groups. These modified resins exhibited excellent hydrophilicity and a lesser dependence on wetting prior to extraction. The synthesis of the *o*-carboxybenzoyl derivative of PS-DVB can be carried out by using phthalic anhydride as acylating agent. Masqué *et al.* (1998) modified PS-DVB with an *o*-carboxybenzoyl moiety to be used in the on-line SPE of some pesticides and phenolic compounds from aqueous samples to obtain better breakthrough volumes and higher recoveries than other commercial sorbents. Yang *et al.* (1996) developed a HPLC ion-exchange stationary phases from the PS-DVB matrix by applying a

hydrophilic coating on the surface. The columns packed with this new packing material exhibit both high chemical stability and high column efficiency that is equivalent to that of silica-based packing materials.

**Table 2.1:** Modifier of the PS-DVB<sup>\*</sup>

Group	Structure
Acetyl	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—CH}_3$
Hydroxymethyl	$\text{—CH}_2\text{OH}$
Benzoyl	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}\text{C}_6\text{H}_5$
2,4-dicarboxylbenzoyl	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}\text{C}_6\text{H}_3(\text{COOH})_2$
<i>o</i> -carboxybenzoyl	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}\text{C}_6\text{H}_4(\text{COOH})_2$
Sulfonate	$\text{—SO}_3^-$
Trimethylammonium	$\text{—CH}_2\text{—N}(\text{CH}_3)_3^+$

<sup>\*</sup> (León-González and Pérez-Arribas, 2000)

Klingenberg and Seubert (2002) showed that introduction of permanently bonded sulfonic acid groups onto PS-DVB resins produce strong cation-exchanger which are stable over a wide range of solvent composition and pH. The resins are stable over a pH range of 0-14, inert against oxidizing reagents such as nitric acid and stable against fluoride and hydrofluoric acid. Since sulfonate and trimethylammonium derivatives are frequently used as ion exchangers in chromatography and preparative analysis, they are easily commercially available under different names and characteristics. Typical commercial phases are Hamilton PRP-X200, Amberlite IRA200, Dowex DR-2030, Sep IC-H (Lida) or NovoClean IC-H (Alltech) for sulfonate cation-exchange resins, and Hamilton PRP-X100, Amberlite IRA-900, Dowex 11 or Sep IC-OH (Lida) for trimethyl-ammonium anion-exchange resins.

Another modified polymer also used for SPE of highly polar compounds is an anion exchanger based on the commercial MFE-Polymer, which is a polymer of the hydroxyethylmethacrylate (HEMA) containing quaternary ammonium functional groups. This sorbent, with particle size of 50  $\mu\text{m}$ , has been packed in a  $150 \times 4.5$  mm conventional LC chromatographic column, and its efficiency to preconcentrate phenoxy acid herbicide residues has been studied. Bacquet *et al.* (1992) has described the chlorosulfonation of styrene-divinyl benzene copolymer characterized by a modification of the textural parameters. The copolymer specific surface area was initially low, and on chlorosulfonation treatment, decrease to a value of  $1 \text{ m}^2 \text{g}^{-1}$ , characteristic of unswollen gel type resins.

## 2.2 Suspension Polymerization

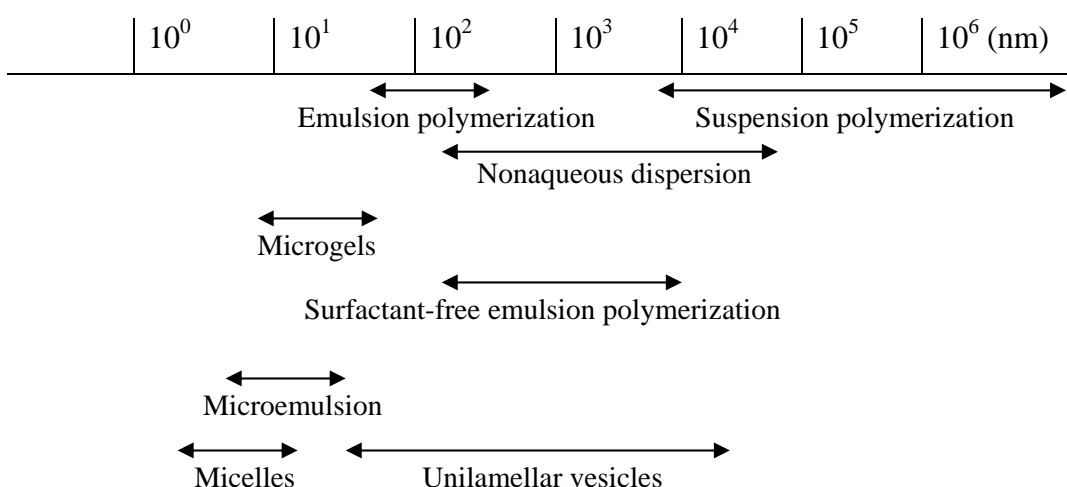
A suspension polymerization is a heterogeneous process, in which slurry of polymer beads is formed by polymerization of a dispersed phase in a continuous medium. The range of particle size covered by each technique is shown in Figure 2.1. The dispersed phase consists of monomer, initiator, chain-transfer agent, and possibly solvent or blowing agent (porogen), the latter to control the porosity of the



beads (Matyjaszewski and Davis, 1998). In general the continuous phase is water, which guarantees on reactor-scale basis proper heat and mass transfer due to its high heat capacity and thermal conductivity, and a low overall viscosity. This overcomes problems that are generally encountered in homogenous polymerization processes at higher monomer conversions, specifically, a runaway of the reaction as a result of the gel effect.

In suspension polymerization a catalyst is dissolved in the monomer, which is then dispersed in water. A dispersing agent is added separately to stabilize the resulting suspension (Allcock *et al.*, 2003; Dyson, 1987). The rate of polymerization and other characteristics are similar to those found in bulk polymerization. Some common dispersing agents are polyvinyl alcohol, polyacrylic acid, gelatin, cellulose, and pectins. Inorganic dispersing agents are phosphates, aluminum hydroxide, zinc oxide, magnesium silicates, and kaolin (Sandler and Karo, 1974).

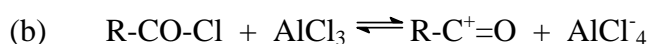
Benefits of suspension polymerization over emulsion polymerization are that in general fewer additives are used and that the final product (average particle sizes  $\sim 10\ \mu\text{m} - 5\ \text{mm}$ ) is easily recovered, after stripping of monomer, solvent/blowing agent, via centrifugation (Matyjaszewski and Davis, 1998). Important commercial suspension polymerization processes include the preparation of poly(vinyl chloride), crosslinked polystyrene resins, and expandable polystyrene.



**Figure 2.1** Typical particle sizes obtained in heterogeneous polymerization techniques (Matyjaszewski and Davis, 1998)

### 2.2.1 Modification Using the Friedel Crafts Acylation Reaction

Anhydrous aluminum chloride ( $\text{AlCl}_3$ ) is a powerful electrophilic catalyst (Lewis acid) and associates with the halogen atom of either an acyl halide or an alkyl halide. In so doing it generates a cation. Depending on its origin, the cation is called a carbonium ion (from an alkyl halide) or an acylium ion (from an acyl halide). The formation of these species is illustrated in Figure 2.2. Both species is particularly stable and reaction with the aromatic hydrocarbon is rapid.



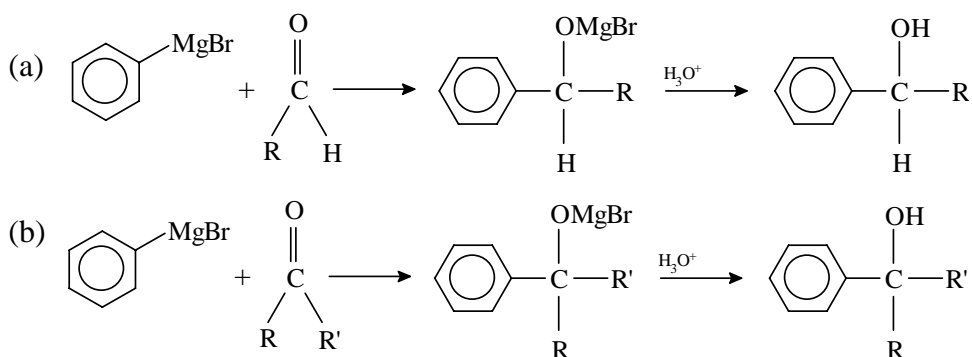
**Figure 2.2** Formation of cation species (a) a carbonium ion (from an alkyl halide), (b) an acylium ion (from an acyl halide) (Durst and Gokel, 1980; Olah, 1973)

One of the modifications of PS-DVB resins in this project is based on Friedel Crafts acylation reaction. The driving force for the reaction is the initial formation of the strong bond between aluminum chloride and the chlorine of benzoyl chloride or between aluminum chloride and the oxygen of acetic anhydride. Aluminum is an electropositive element and chlorine (or oxygen, if the anhydride is used) is an electronegative element, and the bond strength allows the acylium ion to form, but it is itself very unstable and initiates the reaction with the electron-rich aromatic species.

A very wide variety of aromatic ketones can be prepared by the Friedel Crafts acylation. The acylating agent may likewise be any of a wide variety of acid derivatives. Aliphatic as well as aromatic acid chlorides are excellent reaction partners for aromatic hydrocarbons in the Friedel Crafts reaction, which allows much structural variation in the ketones synthesized.

### 2.2.2 Modification Using the Grignard Reagent

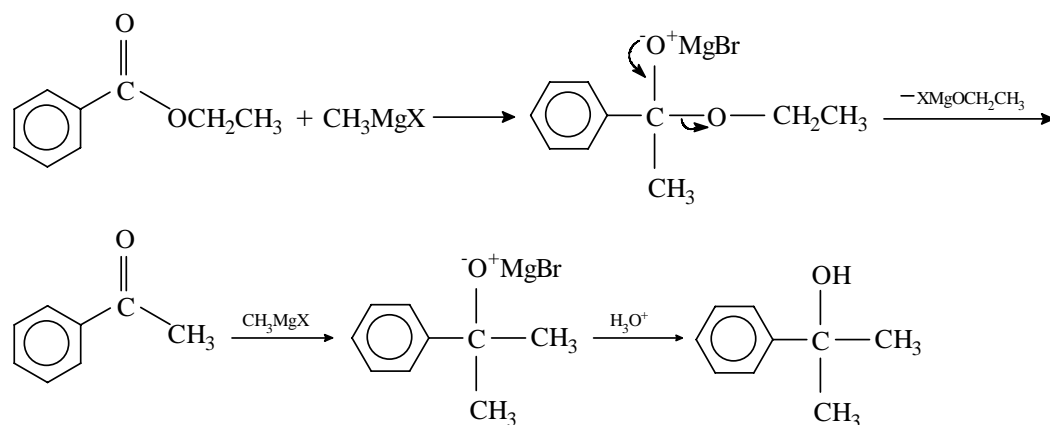
The carbonyl group is particularly versatile because it may have carbon substituents on both sides (ketones) or a carbon substituent on one side and hydrogen on the other (aldehydes). In addition, the carbonyl group may be adjacent to heteroatoms (as in esters and amides) or it may be attached to a halogen, such as chlorine, in acyl halides (Durst and Gokel, 1980; Olah, 1973). Olah, (1973), Durst and Gokel (1980) discovered that reagent behaved as if there were a negative charge on carbon and a positive charge on magnesium, i.e., almost as if the compound were a carbanion salt ( $R-M^+$ ). The addition of the Grignard reagent to an aldehyde or ketone is, in a sense, limited by the fact that carbon and hydrogen are poor leaving groups. As a consequence, only one equivalent of Grignard reagent adds to each carbonyl. When an aldehyde reacts with a Grignard reagent, a secondary alcohol results; ketones yield tertiary alcohols (Figure 2.3).



**Figure 2.3** The addition of the Grignard reagent to (a) an aldehyde, (b) ketone (Durst and Gokel, 1980; Olah, 1973)

Addition of a Grignard reagent to either an ester or ketone carbonyl begins in the same way. The intermediate species in the ester reaction loses alkoxide, forming a ketone during the reaction. This ketone rapidly adds a second mole of Grignard reagent, producing a tertiary alcohol. Two of the substituents in the product are identical, because both are derived from the Grignard reagent. This process is

illustrated in Figure 2.4 for the reaction of a methyl Grignard reagent with ethyl benzoate.



**Figure 2.4** Formation of Grignard reaction (Durst and Gokel, 1980; Olah, 1973)

This destruction of a Grignard by an acid is called the Zerewittenoff reaction and has been used historically to analyze for the presence of acidic hydrogens. Ethers are usually the favored solvents for Grignard reactions. Ethers like diethyl ether or tetrahydrofuran (THF) are good solvents for Grignard reagents and fairly easy to dry. They are also nonacidic. If a Grignard reaction is to be successful, moisture must be rigorously excluded from both the solvent and starting materials. The presence of either water or acid may significantly reduce the yield in the Grignard reaction (Durst and Gokel, 1980; Olah, 1973).

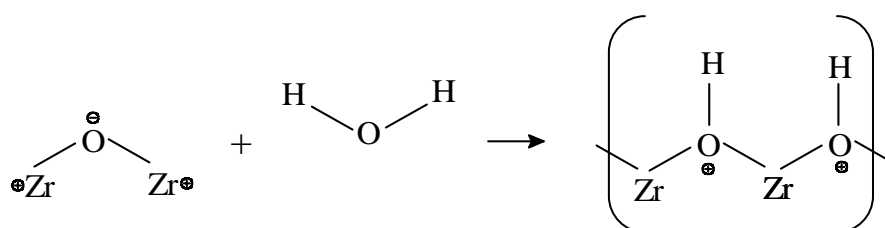
### 2.3 Physical and Chemical Properties of Zirconia

Zirconium occurs widely in the lithosphere (about 0.02%) in the form of zircon ( $\text{ZrSiO}_4$ ), baddeleyite ( $\text{ZrO}_2$ ) and complex oxides and silicates. The principal producers of zirconium minerals are the United States, Australia and Brazil, although

significant deposits are found in India, Malaysia and the USSR. Small concentrations of oxygen, nitrogen, carbon or hydrogen cause embrittlement of metallic zirconium (Clark *et al.*, 1975).

Zirconia ( $\text{ZrO}_2$ ) can be obtained by thermolysis of zirconium salts. Thermal decomposition of zirconium sulphate at  $1000^\circ\text{C}$  leads to a mesoporous material with high surface area ( $90 \text{ m}^2\text{g}^{-1}$ ). Decomposition of  $\text{Zr}(\text{NO}_3)_4$  at  $500^\circ\text{C}$  in the presence of  $\text{H}_3\text{PO}_4$  leads to amorphous, highly acidic zirconia with specific surface area of  $290 \text{ m}^2\text{g}^{-1}$  (Nawrocki *et al.*, 1993; Blumenthal, 1958). Zirconia is available in four forms: amorphous, tetragonal, cubic and monoclinic. The optical, thermal and electrical properties of the zirconia depend on its structure, therefore there is no doubt that zirconia's chromatographic properties will depend on its crystallinity (Aiken, 1990).

All surface zirconium atoms are Lewis acids and all oxygen atoms are Lewis bases. The basic and acids sites are contiguous. The surface layer is usually formed in the presence of other substances like water and oxygen. When molecules are available, the surface will be covered by hydroxyls as each surface Lewis acid-base pair will likely interact with a water molecule as shown in Figure 2.5 (Nawrocki *et al.*, 1993).



**Figure 2.5** Reaction of water molecule with zirconia surface (Nawrocki *et al.*, 1993)

The surface hydroxyl groups on zirconia control the surface chemistry (Vendula and Spencer, 1991). The presence of acidic and basic groups on the surface of zirconia is reflected in its cation and anion-exchange properties. Zirconia has anion exchange properties in neutral and acid solution and cation exchange

properties in alkali solutions (Rigney *et al.*, 1990). Figure 2.6 shows the bridging hydroxyl, being strongly polarized by two zirconium (IV) ions will be more acidic while terminal hydroxyls more basic.



**Figure 2.6** The bridging hydroxyl, being strongly polarized by two zirconium (IV) ions (Rigney *et al.*, 1990)

Nawrocki *et al.* (1993) reported that zirconia shows no detectable dissolution across the entire pH range during 15 days of exposure, whereas a significant amount of alumina is dissolved under the same conditions. The chemical stability contrast between zirconia and silica would be even greater, because silica is more soluble than alumina at pH levels higher than neutral.

### 2.3.1 Zirconia as a Stationary Phase

The zirconia surface has to be modified because it contains many adsorption sites and is able to ion and ligand exchange. We can take advantage of the chemical reactivity of the surface to ‘tailor’ it according to our needs. Generally there are three classes of surface modification of zirconia: (a) dynamic chemical modification- when a mobile phase containing a strongly interacting Lewis base is used, (b) permanent, chemical modification- e.g. silylation of the surface and (c) physical screening e.g. coating the zirconia surface with a polymer or carbon layer.

Since the surface of zirconia is highly heterogeneous, modification of zirconia on the surface to create ion-exchangable, hydrophobic and hydrophilic type phases has been investigated (Hu *et al.*, 2001; Rigney *et al.*, 1990). Mixed oxides have been used widely as catalysts, but very little attention has been paid to their application in chromatographic stationary phases. Considerable attention has been focused on modifying zirconia with inorganic oxides by using sol-gel technique for improvement of its physicochemical properties.

Ceria, as a common rare earth oxide, has comparable chromatographic advantages to zirconia, such as high mechanical strength, thermal and chemical stability. Moreover, both ceria and zirconia are quadrivalent metal oxides, which affords the possibility for them to stoichiometrically match better, leading to homogeneity of the mixed oxides. Hu *et al.* (2001) successfully synthesized ceria-zirconia by the sol-gel process as a new packing material. In comparison with zirconia, ceria-zirconia composite has a higher specific surface area and appropriate pore structure. Results showed the stationary phase was promising for the separation of basic compounds. The new packing material of reversed-phase performance can be prepared by modification of ceria-zirconia with stearic acid, which is available for separation of neutral and basic compounds (Hu *et al.*, 2001).

When coated with a thin layer of polybutadiene, zirconia becomes a reversed phase that is able to withstand extended exposure to mobile phases at pH 14 at a flow rate of  $1 \text{ mL min}^{-1}$  and column temperatures as high as  $200^{\circ}\text{C}$  (McNeff *et al.*, 2000). The extraordinary thermal stability of this type of column enables rapid analysis of a series of chlorophenols at  $200^{\circ}\text{C}$  in a purely aqueous mobile phase. The separation on the polybutadiene-coated zirconia phase column was achieved in less than half the time required by one of the silica columns and at pH 12, which is inaccessible on conventional  $\text{C}_{18}$  silica phases.

### 2.3.2 Polybutadiene-coated Zirconia

Chemically stable modification of chromatographic of zirconia was accomplished by deposition and cross-linking of polybutadiene (PBD) as in the manner for the modification of silica and alumina (Vogelsang *et al.*, 1984). The result is a remarkably stable reversed-phase support. Analysis of the column effluent for zirconium by ICP-AES showed no measurable level of zirconium. Under these same conditions, a commercial polybutadiene-modified alumina column failed due to bed collapse after 8,000 column volumes (Rigney *et al.*, 1989).

The stability of polybutadiene-modified zirconia and alumina was evaluated by exposing columns packed with these supports to a mobile phase of 1 M sodium hydroxide at 100°C. No zirconium was found in the column effluent. In contrast, alumina dissolves to a significant extent during the first hour of exposure to these conditions. In fact, after 3.25 hours of exposure, the amount of aluminium dissolved corresponded to more than 10% of the alumina originally present in the column.

There was evidence of strong, irreversible interactions between certain solutes and the zirconia support. In fact these interactions were expected based on considerations of zirconia's unique surface chemistry. For example, carboxylic acids and organophosphate solute irreversibly adsorbed. These interactions are analogous to the well known interactions of amines with an acidic silica surface. Such interactions lead to problems with peak tailing, poor efficiency, low recoveries and hysteresis effects. These data leads us to believe that some of the surface sites are still available for interactions.

By taking advantage of the strong interaction of phosphates with zirconia, the number of sites could be measured in static adsorption experiments. Even the thickest layer of PBD allowed about  $2.3 \mu\text{mol m}^{-2}$  of phosphate to bind to zirconia. Also chromatographic results confirm that a part of  $\text{ZrO}_2$ -PBD surface is not covered by the polymer. This leads to a mixed-mode retention mechanism. One possible strategy for inhibiting interactions with zirconia's surface is the use of phosphate-containing mobile phases. Chromatography on  $\text{ZrO}_2$ -PBD can be improved by the



addition of phosphate to the mobile phase. This is in contrast with the observed “substantial deactivation” of silicas coated with PBD .

### 2.3.3 Polystyrene-coated zirconia

Particles of zirconia coated with polystyrene were used to separate several mixtures of basic compounds with mobile phase containing  $\text{HNO}_3$  or  $\text{NaOH}$ . The separations of acidic compounds showed lower efficiency even in the presence of an acidic mobile phase.

### 2.3.4 Carbon-coated zirconia

Carbon packings differ substantially from other reversed-phase supports. They are commonly more retentive towards polar compounds and are often more selective for the separation of isomers and homologues (Knox *et al.*, 1983). They also have a much greater chemical stability over a wider pH and temperature range than bonded phases. The drawbacks of carbon packings are often one or more of the following: poor mechanical stability, low surface area, a heterogenous surface (and therefore low loading capacity) and non uniform pore structure.

Zirconia particles coated with a carbon layer developed by Rigney *et al.* (1990) seem to be substantially different from other carbon supports. The process of carbon coating is carried out by passing organic vapors over the zirconia particles at an elevated temperature and reduced pressure. The most common conditions are  $700^\circ\text{C}$  and 5-10 Torr. This procedure creates a uniform carbon coating on porous particles. It is possible to cover more than 97% of the available zirconia surface (Weber and Carr, 1990).

### 2.3.5 Polymer-coated carbon-clad zirconia

When the carbon clad zirconia is covered by a polymer, some of the unique properties of the carbon-clad material are lost. This is due to the mechanism of retention changing from an “adsorption-like” process on the carbon surface to more “partition-like” process in the polymer film. The resulting phase can be considered as composite material with high chemical and mechanical stability. Polymer coating greatly alters the characteristics of carbon-clad zirconia. The solute-adsorbent interactions are significantly weakened. However, polymer coating improves the efficiency of the packing and the mass transfer characteristics. The chemical stability has proven to be remarkable. It withstands 2,000 column volumes of methanol-water (50:50) pH 12 mobile phase at 80°C with no measurable loss of carbon (Weber and Carr, 1990). Generally, polybutadiene coating improves the performance of the carbon-clad zirconia columns, decreases retentivity and increases loading capacity. However, some selectivity is lost.

## 2.4 Solid Phase Extraction

The principal objectives of sample preparation for chromatographic analysis are dissolution of the analytes in a suitable solvent and removal from the solution of as many interfering compounds as possible (Settle, 1997). SPE is widely used for the preconcentration and clean-up of analytical samples, for the purification of various chemicals and for applications such as the removal of toxic or valuable substances from a variety of predominantly aqueous solutions. Typical applications include methods for the determination of trace amounts of pesticides (Pico *et al.*, 2000), determination of trace organic contaminants in water (Marce and Borrull, 2000), analysis of industrial waste waters (Green and Abraham, 2000), determination of azaarenes (Sabik *et al.*, 2000), evaluation of porous polymers (Ensing *et al.*, 2002), isolation of organic compounds from ground water (Yu *et al.*, 2003), sampling of

priority pollutants in waste water (Liska, 2000), collection and concentration of environmental samples in general (Camel, 2003) and, pretreatment of biological samples, such as urine (Safarikova and Safarik, 2002).

For analytical purposes, SPE is usually performed using a small column or cartridge containing an appropriate packing. Also, membranes loaded with appropriate resins and solid phase microextraction (SPME), e.g., for gas chromatographic analysis has been used. In common practice, the adsorbed materials are eluted from the resin with a small amount of organic solvent. The most commonly used material for SPE is chemically bonded silica, usually with a C<sub>8</sub> or C<sub>18</sub> organic group (Fritz *et al.*, 1995).

In the last few years, a series of different polymer-based materials for the SPE of either acidic, neutral or basic compounds out of different sample matrices have been developed. In general, polymer adsorbents have the advantage over bonded silica that they can be used over the entire pH range and the disadvantage that the conditioning of the cartridge is more time consuming. The adsorbent based on PS-DVB phases used in SPE are shown in Table 2.2.

**Table 2.2:** Description of SPE systems with columns (León-González and Pérez-Abbas, 2000)

Adsorbent	Column (height (mm)× ID. (mm)	Conditioning/ washing solvent	Activating solvent	Elution solvent
PS-DVB- acetyl, PS-DVB- hydroxymethyl	8-10 × 6	Methanol, ethyl acetate, acetonitrile	Methanol	Ethyl acetate
PRP X-100	125 × 4	60 mM Nitric acid in 99% methanol	Water at acidic pH	Acetonitrile
PRP X-100	20 × 2	Acetonitrile- NaOH, pH 10	Aqueous NaOH solution	Water
PS-DVB- Benzoyl	10 × 3	Methanol	Water at pH 2.5	Methanol
PS-DVB- Acetyl	10 × 3	Methanol	Water at pH 2.5	Methanol

Chemically bonded silica and porous polystyrene have several shortcomings for their use in SPE. First, while silica itself is hydrophilic and alkaline instable, the hydrocarbon chains make the surface hydrophobic. The consequence is poor surface contact with predominantly aqueous solutions. Second, porous polystyrene resins also have a hydrophobic surface. Third, pretreatment of the SPE materials with an activating solvent such as methanol, acetone or acetonitrile must be used to obtain better surface contact with the aqueous solution being extracted. The activating solvent can be leached out of the resin, thereby causing the extraction to become ineffective. This is especially true if the SPE column becomes dry because air is sucked into the column. The results are reduced capacity and reproducibility. Fourth, many types of organic compounds are incompletely extracted from predominantly aqueous solutions. This problem especially occurs with bonded silica packings. The target of creating new types of chemically bonded resins is to overcome these drawbacks.

For an improvement it has been shown that introduction of polar groups into a PS-DVB resin greatly increases the retention of polar organic compounds. As one of the first, Sun and Fritz (1990 and 1992) modified PS-DVB with alcohol and acetyl functional groups. The modified resins exhibited excellent hydrophilicity and a reduced dependence on wetting prior to solid phase extraction. They also yielded higher recoveries compared to their unmodified homologues. Furthermore, Schmidt *et al.* (1993) shown that also derivatization with other functionalities can be carried out. They used a sulfonated PS-DVB resin for the simultaneous extraction of bases and neutrals.

#### **2.4.1 Basic Principles of SPE**

The SPE method always consists of three to four successive steps (Camel, 2003; Fontanals *et al.*, 2004; Fritz *et al.*, 1995; Hennion, 1999). First, the solid sorbent should be conditioned using an appropriate solvent, followed by the same

solvent as the sample solvent. This step is crucial as it enables the wetting of the packing material and the solvation of the functional groups. In addition, it removes possible impurities initially contained in the sorbent or the packaging. Also, this step removes the air present in the column and fills the void volume with solvent. The nature of the conditioning solvent depends on the nature of the solid sorbent. Typically, for reversed phase sorbent (such as octadecyl-bonded silica), methanol is frequently used, followed with water or aqueous buffer whose pH and ionic strength are similar to that of the sample.

Care must be taken not to allow the solid sorbent to dry between the conditioning and the sample treatment steps, otherwise the analytes will not be efficiently retained and poor recoveries will be obtained. If the sorbent dries for more than several minutes, it must be reconditioned. The second step is the percolation of the sample through the solid sorbent. Depending on the system used, volumes can range from 1 mL to 1 L. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow-rate through the sorbent should be low enough to enable efficient retention of the analytes, and high enough to avoid excessive duration. During this step, the analytes are concentrated on the sorbent. Even though matrix components may also be retained by the solid sorbents, some of them pass through, thus enabling some purification (matrix separation) of the sample.

The third step (which is optional) may be the washing of the solid sorbent with an appropriate solvent, having low elution strength, to eliminate matrix components that have been retained by the solid sorbent, without displacing the analytes. A drying step may also be advisable, especially for aqueous matrices, to remove traces of water from the solid sorbent. This will eliminate the presence of water in the final extract, which, in some cases, may hinder the subsequent concentration of the extract and/or the analysis.

The final step consists of the elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The solvent volume should be adjusted so that quantitative recovery of the analytes is achieved

with subsequent low dilution. In addition, the flow-rate should be correctly adjusted to ensure efficient elution.

#### 2.4.2 Advantages of SPE

Classical liquid-liquid extractions (LLE) of trace elements are usually time-consuming and labor-intensive. In addition, they require strict control of extraction conditions, such as temperature, pH and ionic strength. For all these reasons, several LLE procedures tend to be replaced by SPE methods. SPE technique is attractive as it reduces consumption of and exposure to solvents, their disposal costs and extraction time. In addition, SPE can be interfaced on-line with analytical techniques, such as liquid chromatography (LC) or atomic absorption spectrometry (AAS) (Edward, 1970, Hennion, 1999 and 2000). SPE can be easily automated, and several commercially available systems have been recently reviewed. Home-made systems have also been reported. Its application for preconcentration of trace metals from different samples is also very convenient due to sorption of target species on the solid surface in a more stable chemical form than in solution (Camel, 2003; Liska, 2000; Melo *et al.*, 2004). Upon elution of the retained compounds by a volume smaller than the sample volume, concentration of the extract can be easily achieved. Hence, concentration factors of up to 1000 may be attained (Nilsson, 2000; Coutinho *et al.*, 2004).

SPE allows on-site pretreatment, followed by simple storage and transportation of the pre-treated samples with stability of the retained metallic species for several days. This point is crucial for the determination of trace elements, as the transport of the sample to the laboratory and its storage until analysis may induce problems, especially changes in the speciation (Ensing *et al.*, 2002; León-González and Pérez-Arribas, 2000).

SPE offers the opportunity of selectively extracting and preconcentrating only the trace elements of interest, thereby avoiding the presence of major ions. It may also be possible to selectively retain some particular species of a metal, thereby enabling speciation. This high selectivity may also be used to remove substances present in the sample that may hinder metal determination, such as lipid substances in the case of biological samples (Green and Abraham, 2000; Huck and Bonn, 2000).

## CHAPTER 3

### EXPERIMENTAL

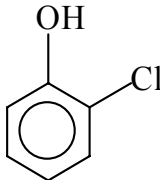
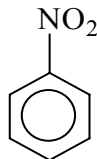
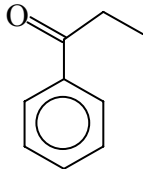
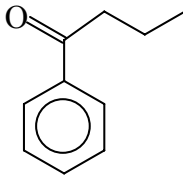
#### 3.1 Material and Test Compounds

Materials used in this research for the preparation and modification of PS-DVB resins are shown in Table 3.1. Table 3.2 describes the test compounds used for SPE.

**Table 3.1:** Description of materials

Materials	Formula molecular	Grade/Purify	Brand
Poly(styrene-divinyl benzene)	$[-C_2H_3(C_6H_5)]_x$ $[-C_{10}H_{10}]_y$	2% cross-linked, 200-400 mesh	Fluka Chemika (Buchs, Switzerland)
Styrene (monomer)	$C_6H_5CH=CH_2$	99% (inhibited with 10-15 ppm 4-tert-butylcatechol)	Fluka Chemika (Buchs, Switzerland)
Divinyl benzene (DVB)	$C_6H_4(CH=CH_2)_2$	80% (inhibited with 1000 ppm p-tert-butylcatechol)	Fluka Chemika (Buchs, Switzerland)
Benzoyl peroxide (BPO)	$(C_6H_5CO)_2O_2$	97%	Fluka Chemika (Buchs, Switzerland)
Poly(vinyl alcohol) (PVA)	$[-CH_2CH(OH)-]_n$	87-89% hydrolyzed	BDH Chemicals (Poole, England)
Polyvinylpyrrolidone (PVP)	$[-CH(C_4H_6ON)CH_2-]_n$	97%	Fluka Chemika (Buchs, Switzerland)
Sodium hydroxide	NaOH	Pellets, 99%	Fluka Chemika (Buchs, Switzerland)
Methanol	$CH_3OH$	99%	Merck (Schuchardt, Germany)
Acetyl chloride	$CH_3COCl$	99%	Kanto Chemical (Tokyo, Japan)
Chloroacetone (chloro-2-propanone)	$ClCH_2COCH_3$	95% (stabilized with 0.5% $CaCO_3$ )	Fluka Chemika (Buchs, Switzerland)
Aluminum chloride anhydrous	$AlCl_3$	99%, $H_2O < 100$ ppm	Fluka Chemika (Buchs, Switzerland)
2-phenyl-2-propanol	$C_6H_5C(CH_3)_2OH$	97%	Aldrich Chemical (Milwaukee, USA)
Zirconyl chloride octahydrate	$ZrOCl_2 \cdot 8H_2O$	99%	Fluka Chemika (Buchs, Switzerland)
Carbon disulphite	$CS_2$	99%	Fluka Chemika (Buchs, Switzerland)



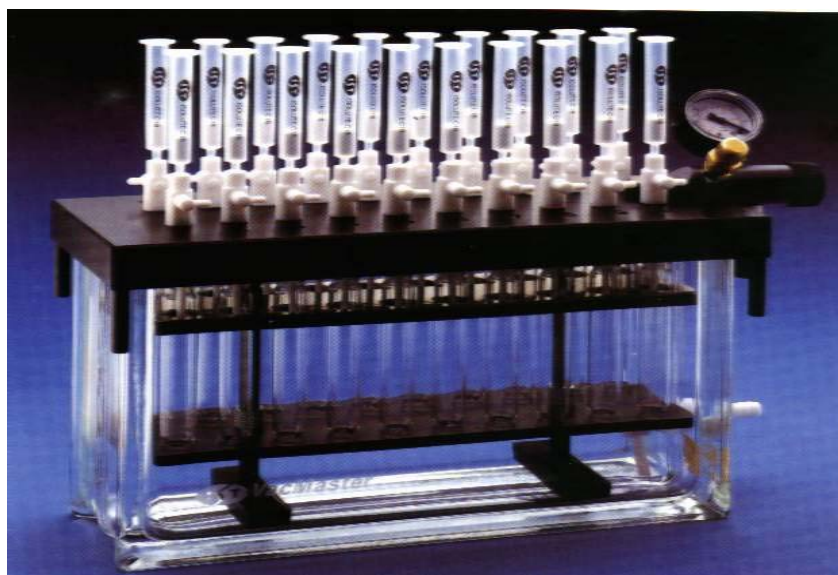
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	99%	Analytical Sciences (Thailand)	
Table 3.2: Description of test compounds and solvents				
Test Compounds/ Solvents	Formula	Structures	Molecular Weight	Brand
2-Chloro-phenol, 98%	C <sub>6</sub> H <sub>5</sub> ClO		128.6	Fluka Chemika (Buchs SG, Switzerland)
Nitro-benzene, 99%	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>		123.1	Merck (Schwarchdt, Germany)
Propio-phenone, 99%	C <sub>9</sub> H <sub>10</sub> O		134.2	Merck (Schwarchdt, Germany)
Butyro-phenone, 99% (Internal standard)	C <sub>10</sub> H <sub>12</sub> O		148.2	Fluka Chemika (Buchs SG, Switzerland)

### 3.2 Instrumentation

A number of instruments were used in this research for the characterization of the synthesized and modified PS-DVB resins. The FTIR spectra were recorded with a Shimadzu-8300 spectrometer (Kyoto, Japan) in the range of 4000-400 cm<sup>-1</sup>. The shape and surface texture of the particles were obtained by a Philips XL-40 scanning electron microscope (California, USA). The samples were coated with gold and observed at 20 KV electron acceleration voltages. The pore size and surface area of

copolymer samples were determined by BJH and BET methods from low temperature nitrogen adsorption isotherms after degassing at 60°C/1.m.Pa for 3 h on a micromeritic apparatus ASAP 2010 (Wellesley, USA).

The thermal gravimetric analyzer (TGA) was conducted using a Mettler Toledo Thermal analyzer (TC-15) (Stockholm, Sweden). The TA controller in air was set at a rate of 12°C min<sup>-1</sup> within a temperature range of 100-800°C. SPE tubes containing home-made adsorbents were tested together with commercial tubes. The commercial SPE tubes used for solid phase extraction were a 6-mL SPE tube pre-packed with 500 mg of C<sub>18</sub> silica adsorbent. In the SPE procedure, the SPE tubes were mounted onto a 10-port VacMaster vacuum manifold (International Sorbent Technology) (Redwood City, USA) connected to an EYELA A-3S Aspirator (Tokyo Rikakikai Co. Limited, Japan) (Figure 3.1). The flow rate of the sample solution was controlled by regulating the air pressure release valve



**Figure 3.1** A SPE vacuum manifold

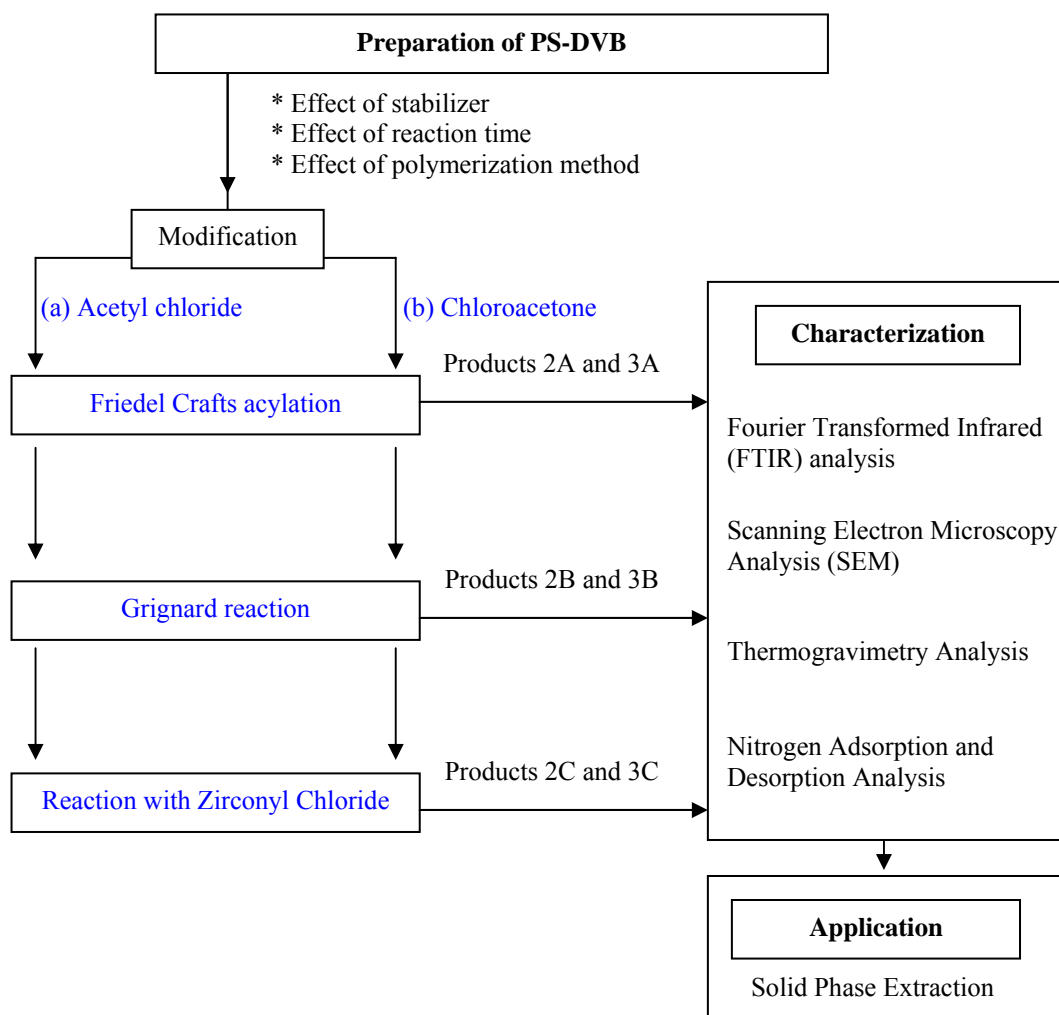
In percentage recovery study, the analytes eluted from SPE tube were collected and then analyzed using a Hewlett Packard Model 6890GC gas chromatography equipped with a flame ionization detector (FID) and a data

processor (Palo Alto, California, USA). The gas chromatographic column used was Ultra-1 932530, a non-polar, fused-silica capillary column (30 m length  $\times$  250  $\mu$ m inner diameter  $\times$  0.20  $\mu$ m film thickness) (Oklahoma, USA). Helium gas was used as the carrier gas with a flow rate of 1.1 mL/min at a pressure of 75 kpa. The injector temperature was set at 250°C and the detector temperature was set at 310°C. The gas chromatography oven was operated under programmed temperature with an initial temperature of 100°C, which was held for 2 minutes and ramped up to 140°C at a rate of 5°C min<sup>-1</sup>. Each sample (1  $\mu$ L) was injected into the gas chromatograph by using a 10  $\mu$ L syringe obtained from Agilent (Little Fall, USA). Triplicate extractions were carried out for each sample and three injections were carried out for each extract to obtain a measure of repeatability.

The efficiencies of adsorbents were determined by determining the percentage of recovery of test compounds by using butyrophenone as internal standard.

### **3.3 Preparation of Adsorbents**

This section discusses about procedures used in the preparation of PS-DVB, and modification of PS-DVB by Friedel Crafts acylation, Grignard reaction and reaction PS-DVB with zirconyl chloride (Figure 3.2).

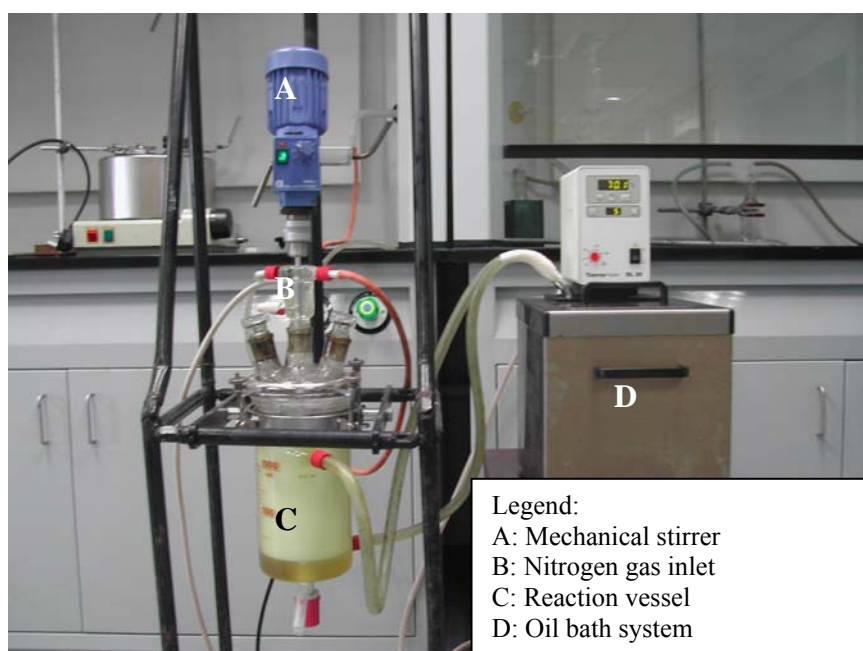


**Figure 3.2** Research framework

### 3.3.1 Preparation of PS-DVB resin

PS-DVB resin was prepared using the method of Mahdavian and Khoei (2002) using a reaction vessel equipped with thermometer and nitrogen gas inlet (Figure 3.3). The reaction vessel was placed in an oil bath set at 70°C. 1.0 g poly vinyl alcohol (PVA) (as stabilizer) dissolved in 500 mL of distilled water were added

to the reactor and stirred until dissolution was complete. The solution was diluted to 1 L using distilled water and after the solution temperature reached 70°C (isothermal conditions), the reactor was purged with nitrogen gas and 9.6 g divinyl benzene (DVB), 120 g styrene and 1.2 g benzoyl peroxide (BPO) were premixed and added to the reactor. The reaction mixture was mechanically stirred for 15 h and then it was filtered off, washed with distilled water and dried. The beads obtained were sieved to separate the 200-400 mesh portion. This part was suspended in 10% aqueous solution of HCl (v/v) and stirred for 1 h at 50°C. It was then filtered, washed with distilled water and dried at 80°C for 12 h.

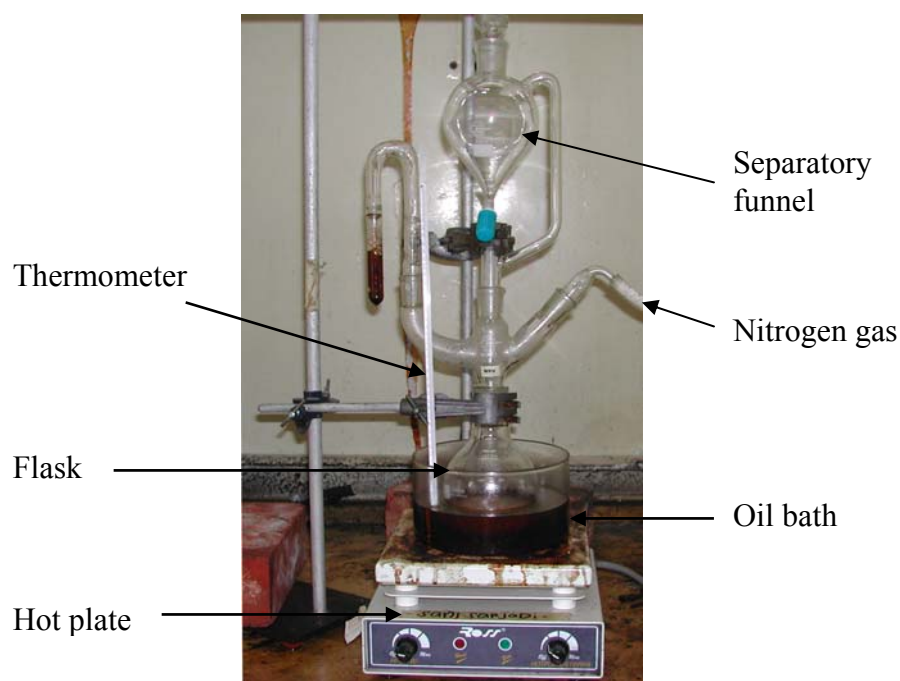


**Figure 3.3** Reactor for polymerization of PS-DVB resin

### 3.3.2 Friedel Crafts acylation of PS-DVB Using Acetyl Chloride and Chloroacetone

The reaction was prepared following the method of Sun and Fritz (1990, 1992). The reaction was carried out using an oil bath system and nitrogen flow

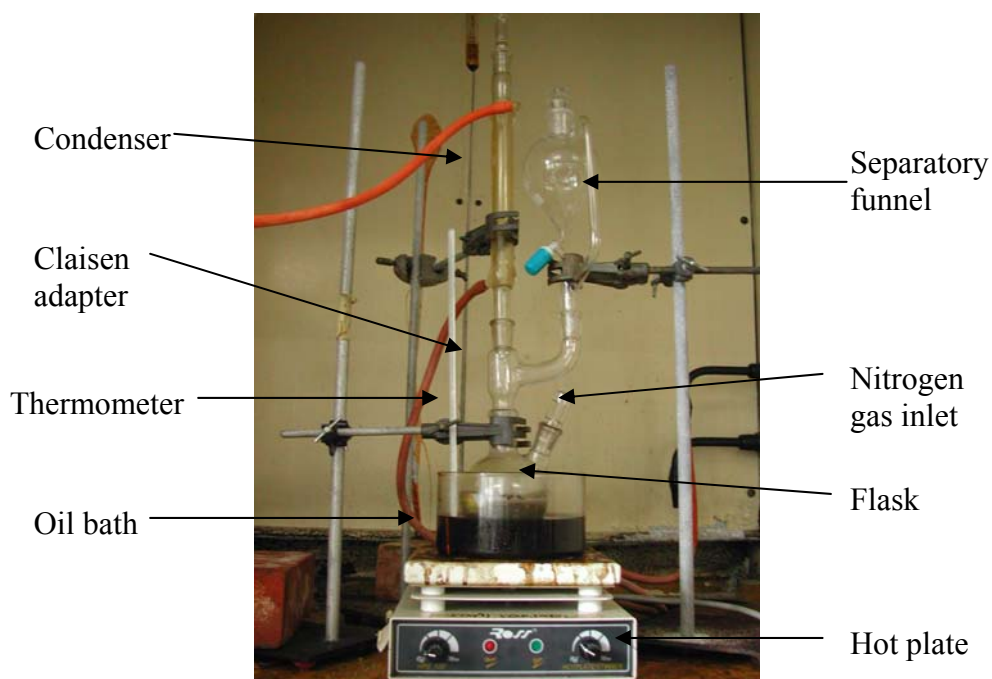
(Figure 3.4). The PS-DVB resin (5.1 g) was poured into the round bottom flask, while the oil bath temperature was set at 50°C. Carbon disulphide (30 mL), anhydrous aluminium chloride (9.5 g) and acetyl chloride (10 mL) was added drop-wise into the mixture. The mixture was kept at 50°C for 24 h and then poured into ice water. The resin was washed with acetone (50 mL), methanol (50 mL) and water (50 mL), consecutively. The yield was dried in an oven and coded as product 2A (*p*-ethanoyl-PS-DVB). Modification of PS-DVB by chloroacetone was carried similarly but use chloroacetone as starting reagent. The resulting produces *p*-2-propanoyl-PS-DVB and was coded product 3A.



**Figure 3.4** System for Friedel Crafts acylation of PS-DVB

### 3.3.3 Modification of *p*-ethanoyl-PS-DVB and *p*-2-propanoyl-PS-DVB by Grignard Reaction

The reaction was carried out using a 250 mL round bottom flask fitted with a stirring bar and Claisen adapter (Figure 3.5). A condenser was fitted into the straight arm of the Claisen adapter, while a separatory funnel was fitted into the bent arm. The round bottom flask was warmed in an oil bath (50°C) and then allowed to proceed by its own heat for 20 minutes. *p*-ethanoyl-PS-DVB (2.0 g) and *p*-2-propanoyl-PS-DVB (2.0 g) were introduced into the flask, respectively. The flask that contained the *p*-ethanoyl-PS-DVB was rinsed with 100 mL of anhydrous diethyl ether and methyl magnesium chloride (10.0 mL) (Grignard reagent) was added. After the addition was complete, the reaction mixture was stirred for an additional 30 min as it slowly reaches room temperature. Distilled water (25 mL) was added to the reaction mixture was added with and the resulting mixture was stirred for 5 min. The reaction mixture was added with 4-5 drops of 3 M sulfuric acid (HCl) to completely dissolve the magnesium salts. At this point there should be two phases (liquid and solid) in the flask. The reaction mixture was transferred to a beaker. The yield was washed with sodium carbonate solution (25 mL) and sodium chloride solution (25 mL), respectively. The reaction produced *p*-2-hydroxyl-2-methylethyl-PS-DVB and *p*-2-hydroxyl-2-methylpropyl-PS-DVB and the yields were dried in an oven and coded as product 2B and 3B, respectively.



**Figure 3.5** System for modification of PS-DVB using Grignard reaction

### 3.3.4 Modification of *p*-2-hydroxyl-2-methylethyl-PS-DVB and *p*-2-hydroxyl-2-methylpropyl-PS-DVB by Zirconyl Chloride

Modification of PS-DVB with zirconyl chloride was carried out using the method of Hussain (1984). For each set of experiment, zirconyl chloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) (10.0 g) was dissolved in 200 mL of freshly prepared distilled water in a 250 mL round bottom flask. The flask was warmed in an oil bath to start the reaction and the reaction was allowed to proceed by its own heat for 20 minutes. *p*-2-hydroxyl-2-methylethane-PS-DVB (5.0 g) was added to the first flask and *p*-2-hydroxyl-2-methylpentane-PS-DVB (5.0 g) added into the second flask. Each mixtures was slowly titrated with 1M solution of sodium hydroxide, addition of the latter being continued until the pH of the resulting solution attained a value of 7.0. The pH of this solution was closely monitored using a pH meter over a period of 24 h to verify that a constant pH had been attained.

The gel formed was separated by using a centrifuge and washed with distilled water (100 mL) until the wash solution was completely free from chloride ions. The gel was then thawed for 24 h at room temperature, filtered and dried under laboratory vacuum at 70°C. The yields were coded as *p*-2-zirconyl-2-methylethyl-PS-DVB chloride and *p*-2-zirconyl-2-methylpropyl-PS-DVB chloride, respectively. All modified PS-DVB resins were coded to reflect their preparation as shown in Table 3.3.



**Table 3.3:** Description of PS-DVB modification

Product	Name	Structure	Reagent
2A	<i>p</i> -ethanoyl-PS-DVB		Acetyl chloride (CH <sub>3</sub> COCl)
2B	<i>p</i> -2-hydroxyl-2-methylethyl-PS-DVB		Methyl magnesium chloride (CH <sub>3</sub> MgCl)
2C	<i>p</i> -2-zirconyl-2-methylethyl-PS-DVB chloride		Zirconyl chloride octahydrate (ZrOCl <sub>2</sub> ·8H <sub>2</sub> O)
3A	<i>p</i> -2-propanoyl-PS-DVB		Chloroacetone (CH <sub>3</sub> COCH <sub>2</sub> Cl)
3B	<i>p</i> -2-hydroxyl-2-methylpropyl-PS-DVB		Methyl magnesium chloride (CH <sub>3</sub> MgCl)
3C	<i>p</i> -2-zirconyl-2-methylpropyl-PS-DVB chloride		Zirconyl chloride octahydrate (ZrOCl <sub>2</sub> ·8H <sub>2</sub> O)

### 3.4 Sample Preparation for SPE-GC Study

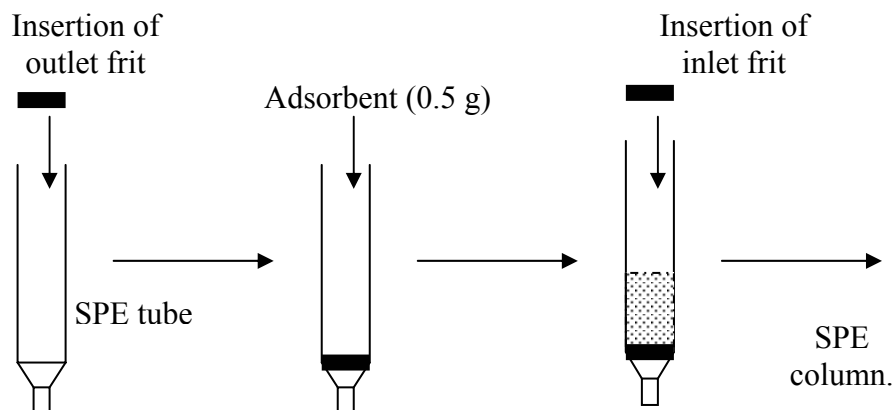
Stock solutions of test compounds 100,000 ppm (10% w/v) were prepared by weighing butyrophenone (2.5 g), 2-chlorophenol (2.5 g), nitrobenzene (2.5 g) and

propiohenone (2.5 g) in separate 25 mL volumetric flasks and each compound was dissolved and diluted in methanol to the mark. The stock solutions prepared were stored in the refrigerator at 4°C. The sample aqueous solution containing individual test compounds for solid phase extraction were prepared by adding 2-chlorophenol 100,000 ppm (10% w/v) stock solution (0.1 mL), nitrobenzene 100,000 ppm (10% w/v) stock solution (0.1 mL) and propiohenone 100,000 ppm (10% w/v) stock solution (0.1 mL) into three separate 10 mL volumetric flasks and each solution was diluted to the mark with deionized water. Each sample of aqueous solution prepared therefore contained 1% v/v of methanol. An aqueous solution of the four test compounds were prepared by adding 2-chlorophenol 100,000 ppm (10% w/v) stock solution (0.1 mL), nitrobenzene 100,000 ppm (10% w/v) stock solution (0.1 mL) and propiohenone 100,000 ppm (10% w/v) stock solution (0.1 mL) into a 10 mL volumetric flask and the solution were diluted to the mark with deionized water. The sample aqueous solution prepared therefore contained (4% v/v) of methanol.

### 3.5 Preparation of Solid Phase Extraction Column

A series of SPE columns were prepared using synthesized adsorbents, namely PS-DVB, *p*-ethanoyl-PS-DVB, *p*-2-hydroxyl-2-methylethyl-PS-DVB, *p*-2-zirconyl-2-methylethyl-PS-DVB chloride, *p*-2-propanoyl-PS-DVB, *p*-2-hydroxyl-2-methylpropyl-PS-DVB and *p*-2-zirconyl-2-methylpropyl-PS-DVB chloride (Table 3.4).

Unmodified and modified PS-DVB adsorbents were ground and sieved into the size range of 400 to 200 mesh by using mortar, pestle and sieve. An empty SPE 6 mL tube was prepared. The outlet frit was inserted until it reaches the bottom base of the SPE tube. Adsorbent (0.5 g) was poured into the SPE tube and the inlet frit was inserted onto the SPE tube so that the adsorbent was sandwiched between the two frits. The steps in the preparation of a laboratory-made SPE column are shown in Figure 3.6.

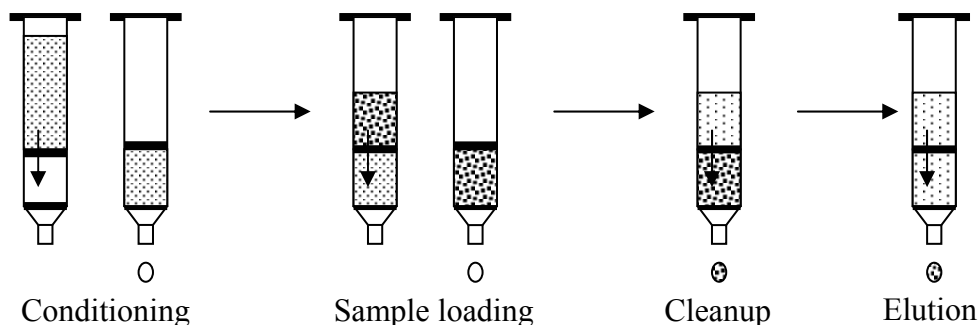


**Figure 3.6** Steps in the preparation of a SPE column

### 3.6 Solid Phase Extraction Procedure

Steps in the SPE are illustrated in Figure 3.7. The SPE was carried out using SPE tube (6 mL) packed with adsorbent (0.5 g). The outlet tip of SPE cartridge was connected to a Vacmaster SPE vacuum manifold equipped with a 10 × 16 mm rack. The SPE cartridge was conditioned and activated by passing methanol (2 mL) followed by deionised water (2 mL) with the aid of a vacuum pump at a flow rate of 1 mL min<sup>-1</sup>. The sorbent was never allowed to dry during the conditioning and sample loading steps. Sample solution (10 mL) containing test compound (1000 ppm) (10% w/v) was passed through the column with the vacuum adjusted to give a flow rate of 1 mL min<sup>-1</sup>. After the sample solution was loaded, the SPE column was rinsed with deionised water (2 mL). Air was drawn through the cartridge for 5 min under increased vacuum to remove excess water. A centrifuge tube (15 mL) was placed below the SPE column and elution was performed using methanol (1 mL × 4 times) at a flow rate of 1 mL min<sup>-1</sup>. Finally, the internal standard, butyrophenone

1000 ppm (10% w/v) was added into the solution and the eluate was made up to 5 mL with methanol. The final solution was analyzed by gas chromatography (GC).



**Figure 3.7** Steps in solid phase extraction

### 3.7 Temperature Programmed GC-FID

The analytes eluted from SPE tube were collected and analyzed using a Hewlett Packard Model 6890GC gas chromatography (GC) equipped with a flame ionization detector (FID) and a data processor. The gas chromatographic column used was a non-polar, fused-silica capillary column, (30 m length  $\times$  250  $\mu$ m inner diameter  $\times$  0.20  $\mu$ m film thickness) Ultra-1 932530. Helium gas was used as the carrier at with a flow rate of 1.1 mL min<sup>-1</sup> at a pressure of 75 kpa. The injector temperature was set at 250°C and the detector temperature was set at 310°C.

The gas chromatography oven was operated under programmed temperature with an initial temperature of 100°C, which was held for 2 minutes and ramped up to 140°C with the rate of 5°C min<sup>-1</sup>. Each sample was injected into the gas chromatograph by using a 10  $\mu$ L syringe (Agilent; USA). The injection volume was 1  $\mu$ L and three injections were carried out for each sample extract to obtained a measure of repeatability.

### 3.8 Determination of Response Factor for the Internal Standard and Test Compounds

The response factors,  $F$ , for internal standard (butyrophenone) and the test compounds (2-chlorophenol, nitrobenzene and propiophenone) were determined by injecting 1  $\mu\text{L}$  of each stock solvent (with a concentration of 100 000 ppm) into the gas chromatograph. Injections were carried out in triplicate to obtain the precision of the analysis. The equations used to calculate the response factor,  $F$ .

$$\text{Response factor, } F = \frac{\text{Peak area}}{\text{Concentration}} \quad (3.1)$$

#### 3.8.1 Determination of the Concentration of the Test Compounds

The concentration of each test compound,  $M_x$  was calculated as shown below.

$$\text{Concentration, } M_x = \frac{F_s}{F_x} \times \frac{A_x}{A_s} \times \text{Concentration, } M_s \quad (3.2)$$

$M_x$  = Test compound concentration (ppm)

$M_s$  = Internal standard concentration (ppm)

$F_s$  = Internal standard response factor

$F_x$  = Test compound response factor

$A_s$  = Internal standard peak area

$A_x$  = Test compound peak area

### 3.8.2 Determination of Test Compound's Recovery Values

The recovery values were calculated as follows:

$$\begin{aligned} \% \text{ Recovery} &= \frac{M_x}{\text{Sample concentration before extraction}} \times 100 \% \times \text{Dilution Factor} \\ &= \frac{M_x}{100,000} \times 100 \% \times 50 \end{aligned} \quad (3.3)$$

where,

$$\text{dilution Factor} = \frac{\text{Volume of sample after extraction}}{\text{Volume of sample before extraction}}$$

$$\text{Dilution Factor} = \frac{5.0 \text{ mL}}{0.1 \text{ mL}} = 50$$

## **CHAPTER 4**

### **RESULTS AND DISCUSSION**

#### **4.1 Preparation of PS-DVB resins**

The final product obtained was white powder PS-DVB copolymer. It was coded as product 1 (see Figure 1.1a). The reaction was carried out by agitating styrene and divinyl benzene with water and the mixture was dispersed into small globules. The chemical reactor was equipped with an agitator which dispersed the water/organic suspension.

#### **4.2 Characterization of Synthesized PS-DVB resin**

Characterizations were carried out on synthesized PS-DVB and the results were subsequently compared with the commercial PS-DVB in order to verify whether the synthesized PS-DVB was successfully produced. The physical characterizations included Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis and nitrogen adsorption-desorption analysis.

#### 4.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

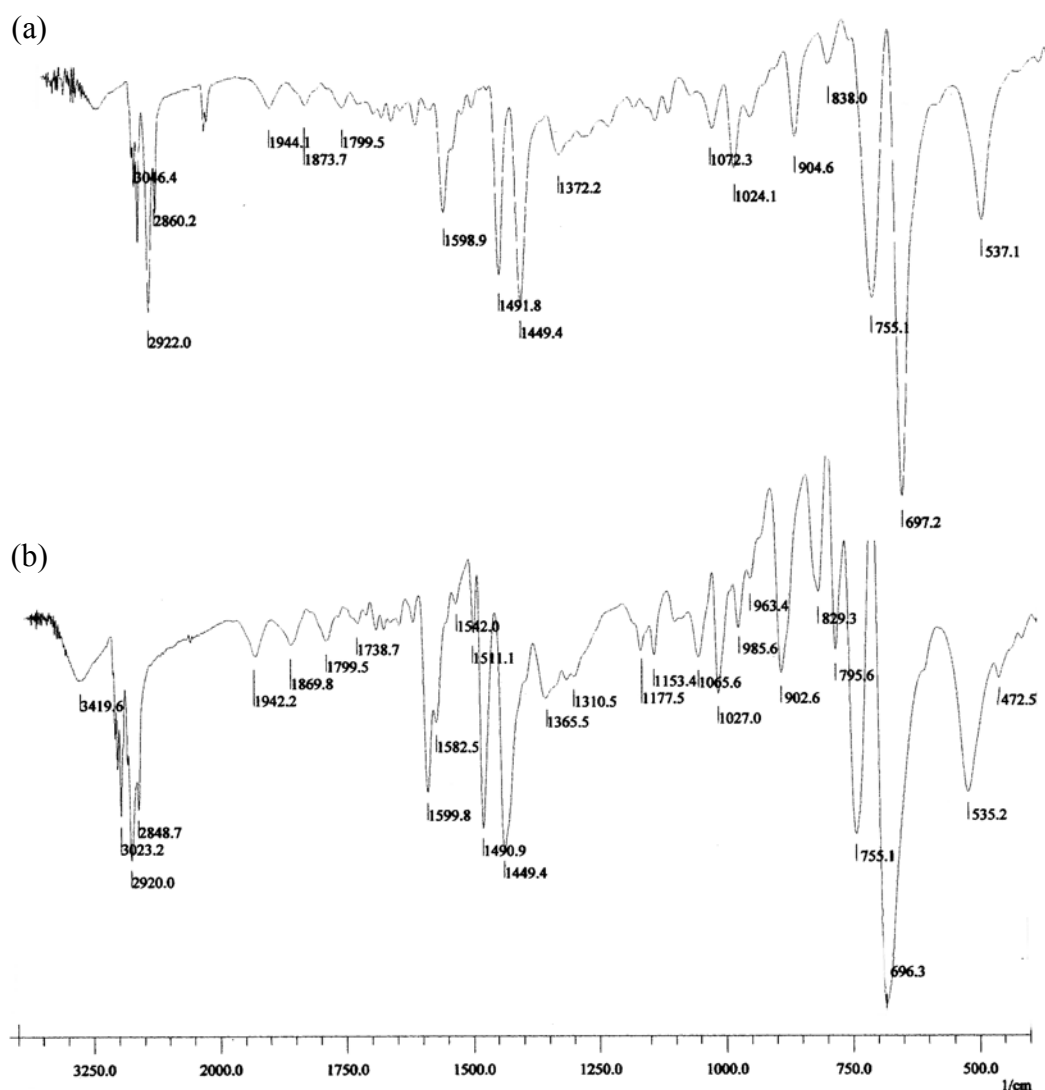
Figure 4.1 shows a FTIR spectrum of synthesized PS-DVB resins and that of commercial PS-DVB for comparison. It can be observed that the FTIR spectrum of the synthesized PS-DVB (Figure 4.1(a)) have similar absorption pattern compared with the FTIR spectrum of commercial PS-DVB resins (Figure 4.1(b)). The finger print region between  $1400\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$  is very important in identifying the compounds. The values and characteristic bands of the compound (Table 4.1) are in agreement with those reported in the literatures (Mahdavian and Khoee, 2002). The results suggests that the synthesized PS-DVB had the same structural properties as the commercial PS-DVB, hence, suggesting that PS-DVB had been successfully synthesized in the laboratory.

The peak at  $3023.2\text{ cm}^{-1}$  is related to the stretching of the aromatic CH bonds from the synthesized PS-DVB resins. Another important peak in the infrared spectra was at  $1599.8$  and  $1490.9\text{ cm}^{-1}$  for the C=C phenyl stretching. The bands close to  $755.1\text{ cm}^{-1}$  and  $696.3\text{ cm}^{-1}$  region are attributed to the presence of out-of-plane bending of mono-substituted benzenes.

**Table 4.1:** Characteristic wave numbers for synthesized PS-DVB resin and commercial PS-DVB resins

Functional Groups	Wave number ( $\text{cm}^{-1}$ )	
	Synthesized PS-DVB	Commercial PS-DVB
=C-H <sub>aromatic</sub>	3046.4	3023.2
-CH <sub>saturated</sub>	2922.0, 2860.2	2920.0, 2848.7
C=C <sub>aromatic</sub>	1598.9, 1491.8	1599.8, 1490.9
Monosubstituted benzene	755.1, 697.2	755.1, 696.3





**Figure 4.1** FTIR spectra of the (a) synthesized PS-DVB resins and (b) commercial PS-DVB resins

#### 4.2.2 Scanning Electron Microscopy Analysis

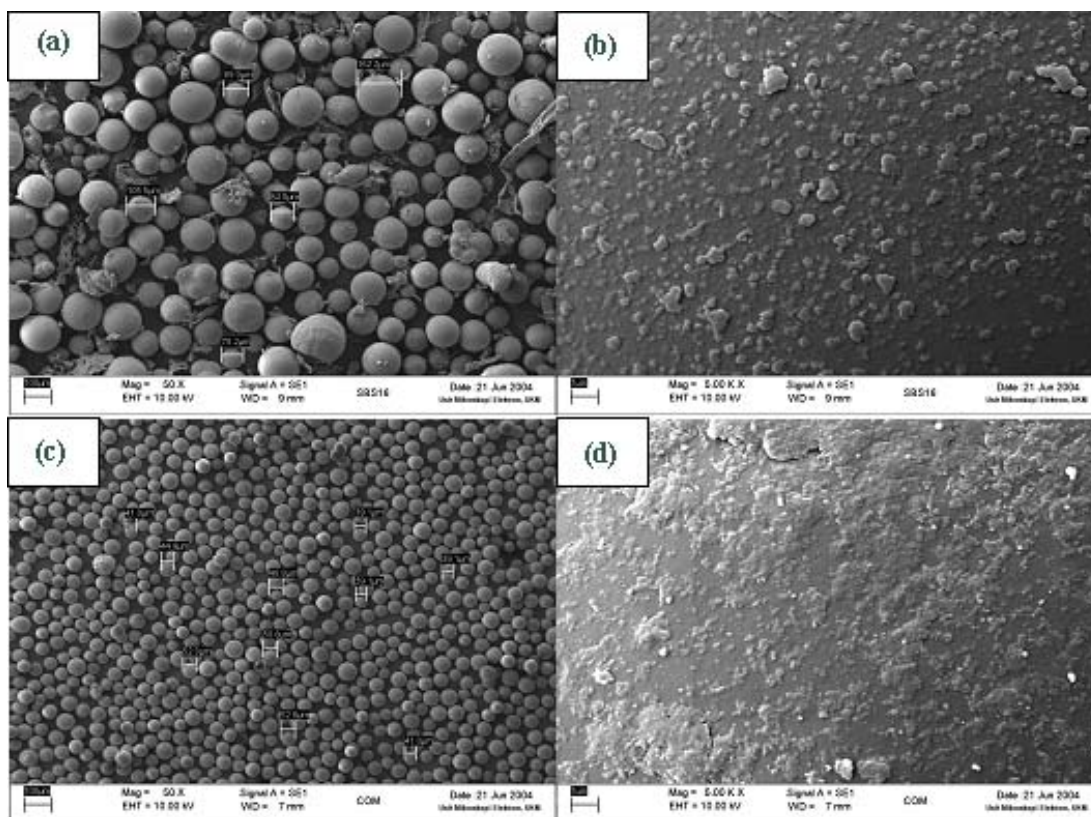
The surface morphology of the sample was determined by scanning electron microscope. Figures 4.2 shows the SEM micrographs of the synthesized PS-DVB and commercial PS-DVB resin have a heterogeneous surface morphology. For the synthesized PS-DVB resin, the average particle size was 104.0  $\mu\text{m}$  as shown in Table 4.2. The particle size of the synthesized PS-DVB resin is relatively larger than

commercial PS-DVB resin. The micrograph (Figure 4.2a) showed that the synthesized PS-DVB resin exhibits non-uniform size and cores with a wide range of particle size from 84.0-162.2  $\mu\text{m}$ . The micrograph of the synthesized PS-DVB resin particles (Figure 4.2b) shows that the surface morphology is smoother and good surface homogeneity. This is probably due to the influence of the controlled polymerization parameters such as the initiator concentration, the stabilizer concentration, the polarity of the polymerization medium, the technique of polymerization used (Tuncel *et al.*, 1993), and the fraction of cross-linking monomer (Maria *et al.*, 2003a).

From the micrograph (Figure 4.2c), the commercial PS-DVB resin consists of sphere beads. The particle size was distributed in a narrow range of 39.1-52.8  $\mu\text{m}$ . There are various factors that influence the particle size of the product; stirring speed is the most important factor that provides a relatively convenient means of particle size control for most practical purposes. The particle size can be controlled by the adjustment of the stirring speed. These limits depend on the size and the configuration of the polymerization reactor (including its stirring arrangement). For the laboratory preparation involving a total volume of about 500 mL, the stirring speed can be varied in the range of 200 to 1000 rpm. The stirring speed of 900 rpm was chosen in this study.

**Table 4.2:** Average particle size of synthesized and commercial PS-DVB resins

<b>Resin</b>	<b>Particle size range, <math>\mu\text{m}</math></b>	<b>Average Particle size, <math>\mu\text{m}</math></b>
Synthesized PS-DVB	84.0-162.2	104.0
Commercial PS-DVB	39.1-52.8	44.9



**Figure 4.2** SEM micrographs of (a) Synthesized PS-DVB resin, magnification  $50 \times$  and (b) magnification  $5000 \times$ ; (c) Commercial PS-DVB resin, magnification  $50 \times$  and (d) magnification  $5000 \times$

However, the synthesized PS-DVB resin particles shown in Figure 4.2a displayed the presence of extra particles probably from the suspension agent during the polymerization process. The case is similar to that reported by Martin *et al.* (2003) for the preparation of the sulfonated metal to PS-DVB resin. They indicated the presence of impurities of tricalcium phosphate (used as the suspension agent in polymerization process) in the polymeric material and the suspension agent was not eliminated by the polymerization process.

### 4.2.3 Thermogravimetry Analysis

Thermogravimetry is a technique whereby a sample is continuously weighed as it heated at a constant and preferably linear rate. The resulting weight change versus temperature curve provides information concerning of the thermal stability and composition of the original sample, the composition and thermal stability of any intermediate compounds and the composition of the residue. In this analysis, five stages of temperature range were observed to study the thermal stability of PS-DVB resin. The temperature range followed from the temperature stage in thermogram (Appendix A). Temperature range less than 135.5°C and range of 135.5-326.6°C are related to low temperature range, while temperature range of 326.6-517.6°C is referred to the intermediate temperature range and temperature range of 517.6-708.6°C and temperature range of 708.6-899.7°C are referred to high temperature stage.

The thermogram for synthesized and commercial PS-DVB resins at various temperature ranges are listed in Table 4.3. At temperature range less than 135.5°C, the resins show weight loss percentages of 1.8% (synthesized) and 1.7% (commercial). Meanwhile, at temperature range of 135.5-326.6°C, the resins show weight loss percentages of 16.8% (synthesized) and 19.1% (commercial). These results reflect that the loss in weight observed over temperature range less than 135.5°C is due to the removal of the loosely bound water from the resin while the loss in weight at temperature range of 135.5-326.6°C corresponds to the removal of more strongly bounded water derived from hydroxyl groups and the decomposition of low-volatility groups.

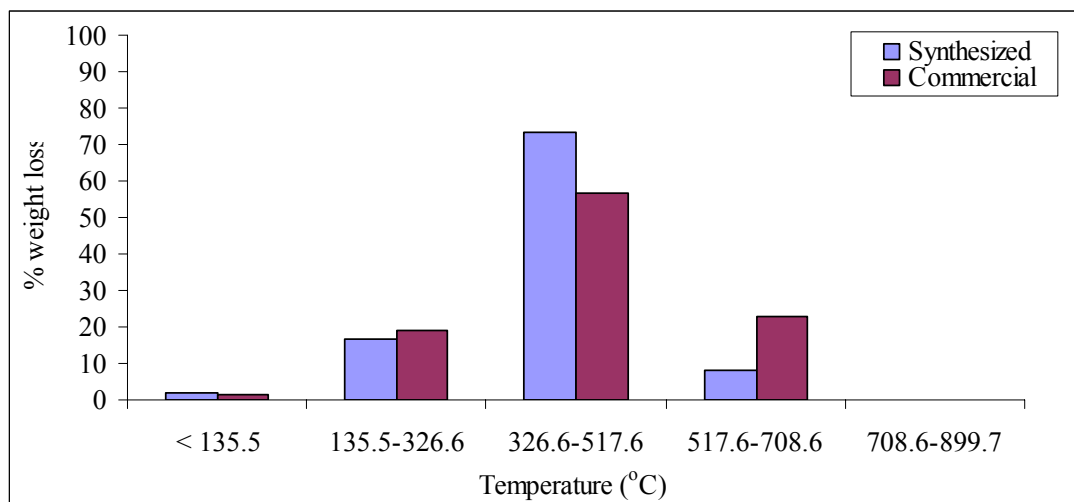
Table 4.3 also indicates that the maximum weight loss for both samples occurs at temperature range of 326.6-517.6°C, 73.5% for synthesized PS-DVB and 56.6% for commercial resin. The decomposition for both PS-DVB resin is completed after the temperature reaches 900°C. It occurs because all of the PS-DVB resins were more unstable during the analysis when the temperature reaches to 708.6°C. The weight loss occurred at the temperature range less than 135.5°C and range of 135.5-

326.6°C, due to dehydration and decomposition of the very low volatile compounds, while the weight lost that occurs at temperature range 326.6-517.6°C, temperature range 517.6-708.6°C and temperature range of 708.6-899.7°C arise from further decomposition of the high volatile groups in the resin.

Figure 4.3 shows the distribution of weight loss percentage of synthesized resin and commercial PS-DVB resin against temperature. The graph presents the percentage of weight loss for all resins that show a similar thermal stability distribution pattern where the percentage of weight loss at temperature range less than 135.5°C is lower than temperature range 135.5-326.6°C. The weight loss percentage has increased due to the decomposition of the most volatile organic compounds exist in the resins. This stage shows that the weight loss percentage of synthesized PS-DVB resin is the highest with 73.5% and the commercial PS-DVB resin present 56.6%. The results indicate that at temperature stage 326.6-517.6°C, the commercial PS-DVB resin is more stable than synthesized PS-DVB resin. The result is affected by the polymerization process.

**Table 4.3:** Thermogravimetric analysis results for synthesized and commercial PS-DVB resins at various temperature ranges

PS-DVB resins	% of weight loss					Residue (%)
	< 135.5	135.5- 326.6	326.6- 517.6	517.6- 708.6	708.6- 899.7	
Synthesized	1.8	16.8	73.5	7.9	0.0	0.0
Commercial	1.7	19.1	56.6	22.7	0.0	0.0

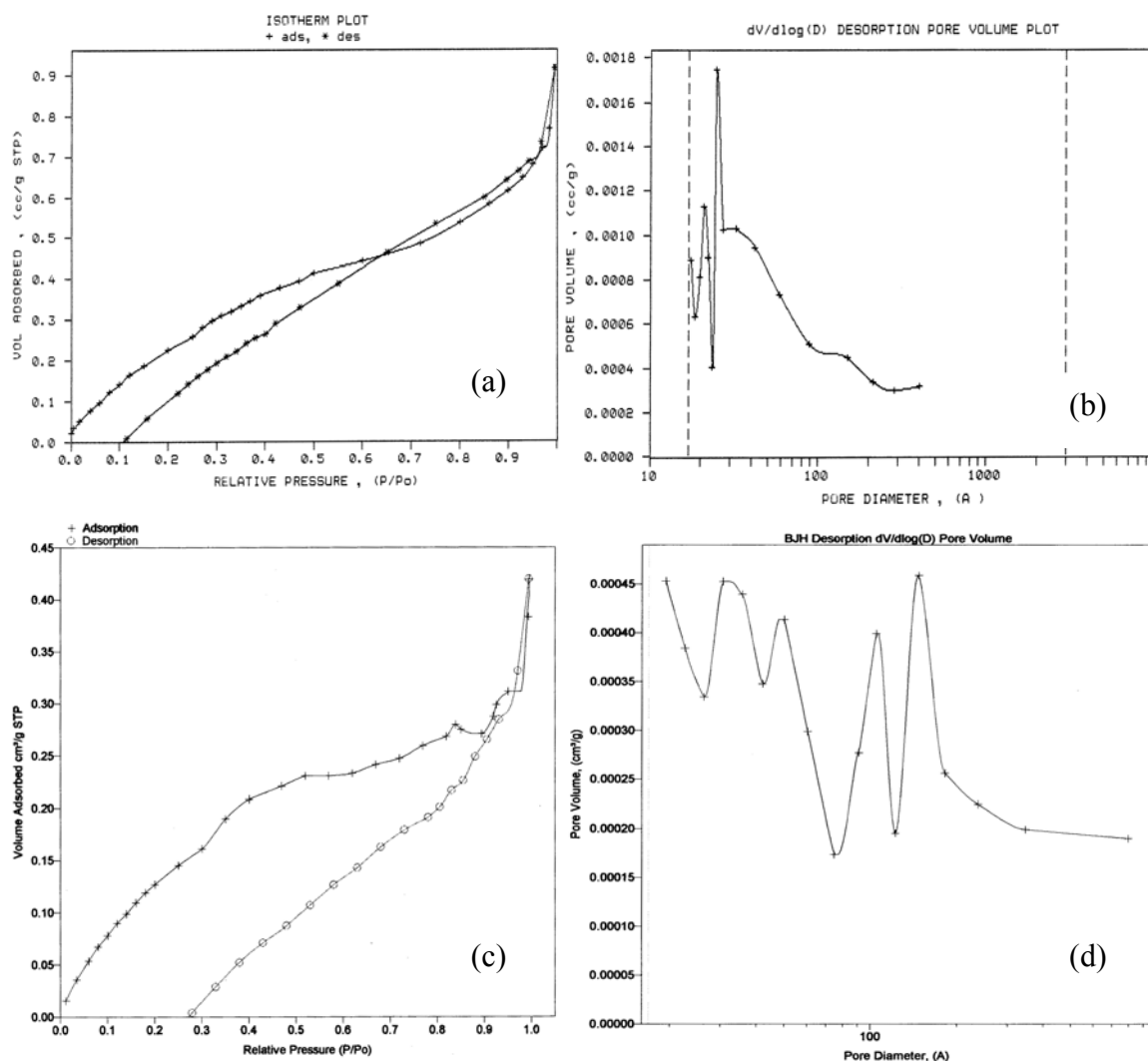


**Figure 4.3** Distribution of weight loss percentage against various temperature ranges for synthesized and commercial PS-DVB resins

#### 4.2.4 Nitrogen Adsorption and Desorption Analysis

Nitrogen adsorption isotherms of synthesized and commercial PS-DVB resins are presented in Figure 4.4. The commercial PS-DVB resin was used as a reference. Both nitrogen sorption isotherms show that the PS-DVB resin was not particularly well-formed of isotherm shape (Figures 4.4a and 4.4c). However, the nitrogen adsorption and desorption isotherms for commercial and synthesized PS-DVB resin show a similar pattern, with the low BET surface area.

The pore size distributions of the synthesized and commercial PS-DVB resins are shown in Figures 4.4b and 4.4d. In the present work, the distribution of pores for the synthesized PS-DVB resin was covered in the range of 20.0-40.0 Å (Figure 4.4b). From Figure 4.4d, it was found that the distribution of pores size for the commercial PS-DVB resin was covered in the range of 20.0-200.0 Å. This result suggests the presence of different sizes of mesopore in the commercial PS-DVB resin. It is also recognized that the commercial PS-DVB resin was distributed in a wide range of mesopore compared to synthesized PS-DVB resin.



**Figure 4.4** (a) Nitrogen adsorption isotherm and (b) average pore size distribution of the synthesized PS-DVB resin; (c) Nitrogen adsorption isotherm and (d) average pore size distribution of the commercial PS-DVB resin

From the Table 4.4, the synthesized and commercial PS-DVB resin show that the BET surface area are 1.2 and 0.7 m<sup>2</sup>g<sup>-1</sup>; average pore volume are  $1.2 \times 10^{-3}$  and  $6.5 \times 10^{-4}$  cm<sup>3</sup>g<sup>-1</sup>; and average pore diameter are 41.3 and 38.0 Å, respectively. These results indicate that the synthesized PS-DVB resin has slightly higher BET surface area; average pore volume and average pore diameter compared to the commercial PS-DVB resin.

**Table 4.4:** Pore and surface characteristic of synthesized PS-DVB resin and commercial PS-DVB resin

PS-DVB Resins	BET surface area ( $\text{m}^2\text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3\text{g}^{-1}$ )	Average pore width ( $\text{\AA}$ )	Type of pore
Synthesized	1.2	$1.2 \times 10^{-3}$	41.3	Meso
Commercial	0.7	$6.5 \times 10^{-4}$	38.0	Meso

#### 4.2.4.1 Effect of Reaction Time

It was found that PS-DVB 5h, PS-DVB 15h and PS-DVB 20h exhibits 3.7, 1.5 and  $1.2 \text{ m}^2\text{g}^{-1}$  for BET surface area, respectively. The result (Table 4.5) suggests that the BET surface area increases with the decrease time of polymerization. The reaction time shows a significant effect to the BET surface area and physical characteristics. It can be observed that when reaction time was set at 5h, the pore width of PS-DVB was approximately 38.7  $\text{\AA}$ . Highest average pore width value and pore volume were obtained when the reaction time was fixed at 15 h with a value of 137.7  $\text{\AA}$ . However, a significant decrease of pore width was noted when the reaction time was increased to 20 h.

**Table 4.5:** Effect of reaction period on nitrogen adsorption analysis data for synthesized PS-DVB.

Reaction time (h)	BET surface area $\text{m}^2/\text{g}$	Total pore volume $\text{cm}^3/\text{g}$	Average pore width ( $\text{\AA}$ )	Physical characteristics
5	3.7	$3.5 \times 10^{-3}$	38.7	White, harder bead.
15	1.5	$5.1 \times 10^{-3}$	137.7	Small, white, powder, easy to grind.
20	1.2	$1.2 \times 10^{-3}$	41.3	



#### 4.2.4.2 Effect of Stabilizer

Table 4.6 shows the poly(vinyl alcohol) has a BET surface area of  $1.2 \text{ m}^2\text{g}^{-1}$  and total pore volume of  $1.2 \times 10^{-3} \text{ cm}^3\text{g}^{-1}$  and polyvinyl pyrrolidone has a BET surface area of  $0.7 \text{ m}^2\text{g}^{-1}$  and average pore volume of  $1.0 \times 10^{-3} \text{ cm}^3\text{g}^{-1}$ . The results show that polyvinyl alcohol was a better stabilizer than polyvinyl pyrrolidone. The particles obtained from poly(vinyl alcohol) polymerization has a smaller size and the material was easy to grind, unlike the material obtained from polymerization that used polyvinyl pyrrolidone. The beads particle size was controlled using a sieve shaker (200-400 mesh portion). It was probably because poly(vinyl alcohol) is incorporated into the surface of the polystyrene beads and thus giving better protection against growing process (Gauthier *et al.*, 2004). The particle size distribution of the PS-DVB resin prepared with poly(vinyl alcohol) as a suspension stabilizer can vary widely by changing the relative amounts of the monomer and aqueous phase. When using poly(vinyl alcohol) in the polymerization of the PS-DVB resin the value of BET surface area, average pore diameter and total pore volume is higher compared to polyvinyl pyrrolidone.

**Table 4.6:** Nitrogen adsorption analysis data for synthesized PS-DVB resin using different stabilizers

Stabilizer	BET surface area $\text{m}^2\text{g}^{-1}$	Total pore volume $\text{cm}^3\text{g}^{-1}$	Average pore width (Å)	Physical characteristics
Poly(vinyl alcohol)	1.2	$1.2 \times 10^{-3}$	41.3	Small, white, powder, easy to grind.
Poly(vinyl pyrrolidone)	0.7	$1.0 \times 10^{-3}$	60.3	Bigger, white, difficult to grind.

#### 4.2.4.3 Effect of Polymerization Method

Table 4.7 shows a significant difference in the data of nitrogen adsorption for the synthesized PS-DVB resin. The surfactant polymerization technique showed that the pore volume and average pore diameter of this sample was lower compared to the seeding polymerization technique. The result obtained suggests that the surfactant polymerization technique was a better method than the seeding polymerization technique.

**Table 4.7:** Nitrogen adsorption analysis data for synthesizing PS-DVB resin by different techniques

Technique	BET surface area $\text{m}^2\text{g}^{-1}$	Total pore volume $\text{cm}^3\text{g}^{-1}$	Average pore diameter ( $\text{\AA}$ )	Physical characteristics
Seeding	2.0	$3.5 \times 10^{-3}$	68.6	Small, white, powder, easy to grind.
Surfactant	1.2	$1.2 \times 10^{-3}$	41.3	

### 4.3 Preparation of *p*-2-zirconyl-2-methylethyl-PS-DVB Chloride

Modification PS-DVB adsorbent was carried out via Friedel Crafts acylation reaction with acetyl chloride using Lewis acid catalyst (product 2A) followed by Grignard reaction of the product with methyl magnesium chloride (product 2B) and reaction with zirconium(IV) oxide chloride octahydrate (product 2C). The polymer adsorbent of product 2A (*p*-ethanoyl-PS-DVB) was prepared using Friedel Crafts acylation reaction with acetyl chloride in the presence of aluminium chloride anhydrous ( $\text{AlCl}_3$ ) as Lewis acid catalyst. The ketone functional group  $\text{CH}_3\text{-CO-}$ (PS-DVB) showed an intense carbonyl absorption band at  $1678.9 \text{ cm}^{-1}$  in the FTIR

spectrum. After that, the product 2A was then converted to product 2B (*p*-2-hydroxyl-2-methylethyl-PS-DVB) using Grignard reaction with methyl magnesium chloride followed by hydrolysis. The product 2A resin was allowed to react with zirconyl chloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) in acetonitrile-water (1:1) mixture to afford the product 2C (*p*-2-zirconyl-2-methylethyl-PS-DVB chloride). The reaction sequence is depicted in Figure 1.1b.

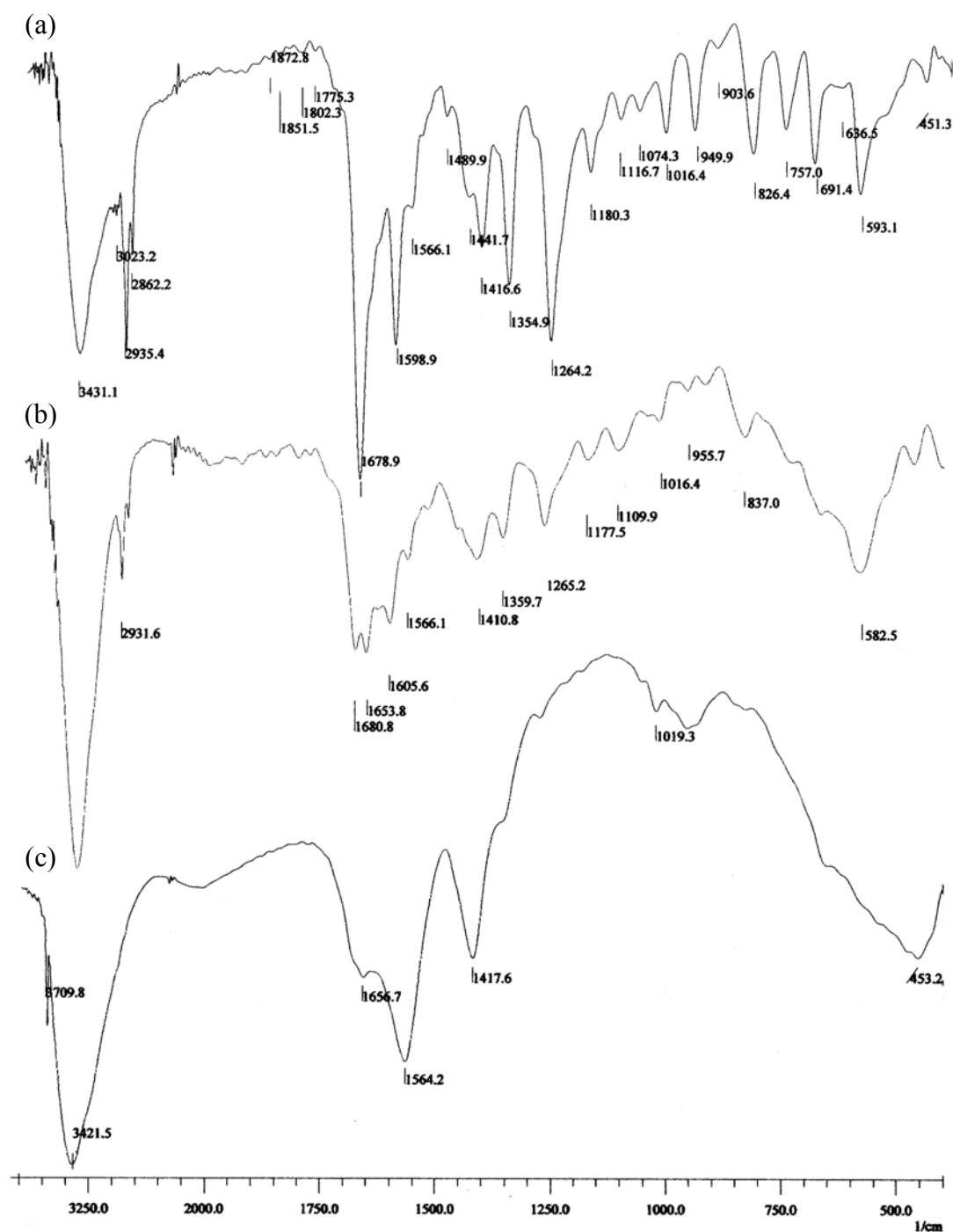
#### 4.4 Characterization of *p*-2-zirconyl-2-methylethyl-PS-DVB Chloride

##### 4.4.1 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR analysis of product 2A in Figure 4.5a shows its peaks at  $2935.4\text{ cm}^{-1}$  and  $3023.2\text{ cm}^{-1}$ . The peaks were assigned to  $\text{C-H}_{\text{alkanes}}$  and  $\text{C-H}_{\text{aromatic}}$  stretching, respectively. Polystyrene functional group shows the stretching bands at  $1872.8\text{ cm}^{-1}$ ,  $1851.5\text{ cm}^{-1}$ ,  $1802.3\text{ cm}^{-1}$  and  $1775.3\text{ cm}^{-1}$ . The  $\text{C}=\text{C}_{\text{aromatic}}$  stretching is observed at  $1598.9\text{ cm}^{-1}$  and  $1416.6\text{ cm}^{-1}$ . The presence of a  $\text{C}=\text{O}$  functional group in the modified phase is proven by a strong band at  $1678.9\text{ cm}^{-1}$ . The para- and mono-substituted benzene rings are observed at  $826.4\text{ cm}^{-1}$  and  $691.4\text{ cm}^{-1}$ ,  $593.1\text{ cm}^{-1}$  respectively. The absorption pattern of product 2A FTIR spectrum (Figure 4.5a) is identical to product 1 resin FTIR spectrum (Figure 4.1a) and it shows strong absorption at  $1678.9\text{ cm}^{-1}$ , indicating the existence of  $\text{C}=\text{O}_{\text{stretching}}$ . It means that the modification of synthesized PS-DVB resin with acetyl chloride was successfully achieved. The FTIR spectrum showed that there was a similarity in the absorption frequencies between synthesized PS-DVB resin and product 2A. Infrared spectrum for product 1 resin was used as a reference for comparison with product 2A.

The FTIR analysis of product 2B resin in Figure 4.5b shows peaks at  $2931.6\text{ cm}^{-1}$  and  $2840.0\text{ cm}^{-1}$ . The peaks were assigned to  $\text{C-H}_{\text{alkanes}}$  stretching. The  $\text{C}=\text{C}_{\text{aromatic}}$  stretching were adsorbed at  $1566.1\text{ cm}^{-1}$  and  $1410.8\text{ cm}^{-1}$ . The presence of OH functional group in the modified phase was proven by a strong band at  $3430.1\text{ cm}^{-1}$ . The para- and mono-substituted benzene rings were observed at  $582.5\text{ cm}^{-1}$  and  $453.2\text{ cm}^{-1}$ . FTIR spectrum obtained for product 2C is depicted in Figure 4.5c. The

result showed that the sample gave similar adsorption bands with product 2B except for the spectrum of product 2C which exhibits an extra broad band. It may be due to the stretching vibration of the  $-OH$  group present in the sample. Table 4.8 summarizes the FTIR absorption data incorporating functional groups from the FTIR spectra of PS-DVB-modified resin.



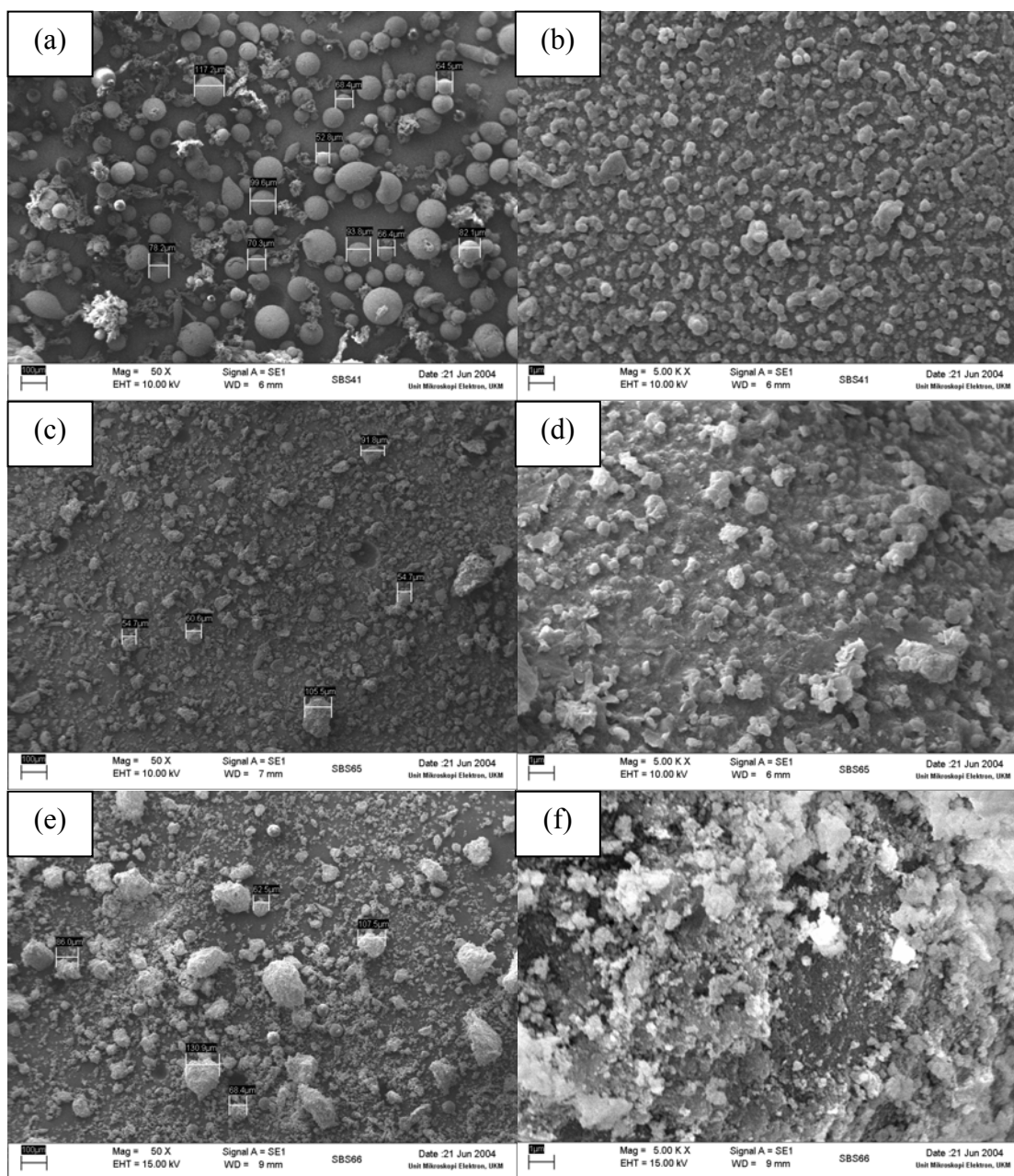
**Figure 4.5** FTIR spectra of the (a) product 2A, (b) product 2B, and (c) product 2C

**Table 4.8:** Absorbance signals for the functional groups of modification PS-DVB using acetyl chloride

Functional Groups	Resin		
	Product 2A	Product 2B	Product 2C
	Wave number, $\text{cm}^{-1}$		
OH	-	3430.1 ( <i>h</i> )	3421.5 ( <i>h</i> )
=C-H <sub>aromatic</sub>	3023.2	-	-
-CH <sub>saturated</sub>	2935.4, 2862.2	2931.6, 2860.0	-
C=O	1678.9	-	-
C=C <sub>aromatic</sub>	1598.9, 1416.6	1605.6, 1410.8	1564.2, 1417.6

#### 4.4.2 Scanning Electron Microscopy Analysis

From the SEM micrograph, it was found that the particle of PS-DVB-modified resin scattered on the surface of the tape in a small size which resembles spherical beads as shown in Figure 4.6. Figure 4.6a shows the surface morphology of the product 2A particle. The surface morphology of the particles showed that they are relatively irregular, mixture of the particle shapes and not fully spherical beads form. A spherical morphology was also observed, although in this case some debris appeared are mixed with the particles. The surface of these particles is rougher compared to the surface of the product 1 resin particles (Figure 4.2b) as observed in Figure 4.6b. These results seem to suggest that the changing of the surface morphology was due to the introduction of product 1 resin particles at an elevated temperature during the Friedel Crafts acylation. In addition, the use of excessive acetyl chloride agent was expected to contribute to the irregularity of beads shape.



**Figure 4.6** SEM micrographs of (a) product 2A; magnification 50 $\times$  and (b) magnification 5000 $\times$  (c) product 2B; magnification 50 $\times$  and (d) magnification 5000 $\times$  (e) product 2C; magnification 50 $\times$  and (f) magnification 5000 $\times$

The arrangement of the product 2B particles is not compact and do not show any specific pattern as shown in Figure 4.6c. The morphology is similar to that observed in product 2A. However, the morphology of the surface of this material is

irregular surface. The surface properties were altered due to the presence of the agent methyl magnesium chloride or through the refluxing process in Grignard reaction.

Figures 4.6e and 4.6f show the micrograph of the product 2C. The arrangement of the particles is not compact and does not show any specific pattern. The surface morphology does not show any specific pattern. This is probably due to the reaction condition in the reflux reaction. The zirconia particles fused into large units, known as aggregates flocculated to form agglomerates. Actually, some beads present a few clusters of inorganic material particles on preferential regions of their surfaces. Based on these initial experiments Maria *et al.* (2003b) proposed that it could be due to the difference in viscosity of the two kinds of composite during the polymerization process. Low energy sites are probably formed around all surfaces of the high viscosity beads, facilitating the sorption of the inorganic material particles. The polymeric layer on the metal particles was also clearly recognizable but, as in the previous cases, it was not possible to determine the thickness (Maria *et al.*, 2003a).

#### 4.4.3 Thermogravimetry Analysis

The thermogravimetric analysis result for PS-DVB-modified resin at various temperature ranges are listed in Table 4.9. The temperature stage A and B show that the product 2C is the highest weight loss percentage compared to the other resins. These results reflect that the loss in weight at the temperature range less than 135.5°C is due to the removal of the loosely bound water from the resin. Meanwhile, the loss in weight at temperature range 135.5-326.6°C corresponds to the removal of more strongly bounded water derived from hydroxyl groups. It is also due to the decomposition of low volatile groups. The result indicates that the product 2C has a high degree of water content in their structure compared to the other resin. Table 4.9 also indicates that the maximum weight loss for most of the sample occurs at the temperature stage 517.6-708.6°C except for product 2C, which occurs at temperature

stage 326.6-517.6°C. The maximum weight loss percentage obtains for product 2A, product 2B and product 2C at temperature stage 517.6-708.6°C (51.3%), 517.6-708.6°C (31.7%) and 326.6-517.6°C (20.1%), respectively. The result demonstrates that the maximum weight loss percentage of the resins in Table 4.9 is in accordance to product 2C < product 2B < product 2A.

In general, the weight loss percentage for the product 2A at temperature stage 517.6-708.6°C is higher (51.3%) than the other resins and the decomposition for product 2A is completed after the temperature reaches 900°C. It occurred because all of the product 2A is unstable compared to the modified resins during the analysis when the temperature reached 708.6°C. The weight loss occurred at temperature range less than 135.5°C and 135.5-326.6°C are due to dehydration and decomposition of the very low volatile compounds. The weight lost occurred at the temperature range 326.6-517.6°C, 517.6-708.6°C and 708.6-899.7°C arises from further decomposition of the high volatile groups in the resin.

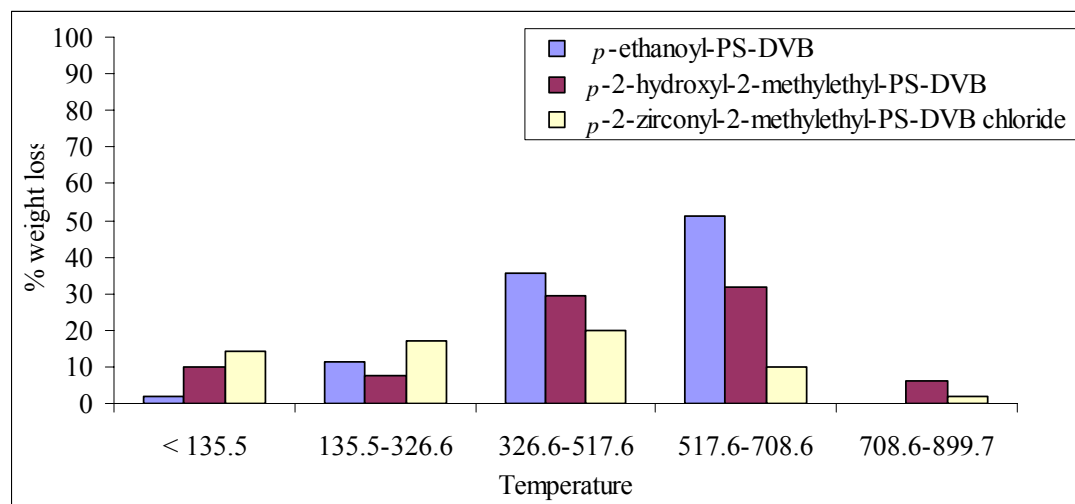
When the temperature reaches 900°C, the residue percentage for product 2A, product 2B and product 2C are 0.0%, 15.0%, and 36.9%, respectively. The percentage of residue of product 2C is higher (36.9%) than the other resins. The total value of the percentage of weight loss of product 2C is 63.1%. This result is affected by the presence of zirconia oxide in the resins during the modification process of PS-DVB resin. The properties changed because of the effect of heat during the Friedel Crafts acylation and Grignard reactions. The result demonstrates that the arrangement of the thermal stability of the resins in Table 4.9 in accordance as product 2A < product 2B < product 2C.

**Table 4.9:** Thermogravimetric analysis results of modified PS-DVB using acetyl chloride at various temperature ranges

Resin	% weight loss					Residue (%)
	< 135.5	135.5-326.6	326.6-517.6	517.6-708.6	708.6-899.7	
Product 2A	2.1	11.2	35.4	51.3	0.0	0.0
Product 2B	9.8	7.7	29.6	31.7	6.2	15.0
Product 2C	14.3	17.0	20.1	10.0	1.7	36.9



Figure 4.7 shows the graph of weight loss percentage of product 2A, product 2B and product 2C against various temperature stages. The graph presents the percentage of weight loss for all resins that show a similar thermal stability distribution pattern where the percentage of weight loss at various temperature range less than 135.5°C, 135.5-326.6°C and 326.6-517.6°C are lower than temperature stage 517.6-708.6°C. Temperature stage 517.6-708.6°C is referred to intermediate temperature range and the weight loss percentage has increased due to the decomposition of the most volatile organic compounds exist in the resins. At this stage, the weight loss percentage of product 2A is the highest (51.3%). The results indicate that at temperature range 326.6-517.6°C, the modified resins are more stable than unmodified resins (Section 4.2.3). The results are affected by the acetyl chloride reagents in the Friedel Crafts acylation.



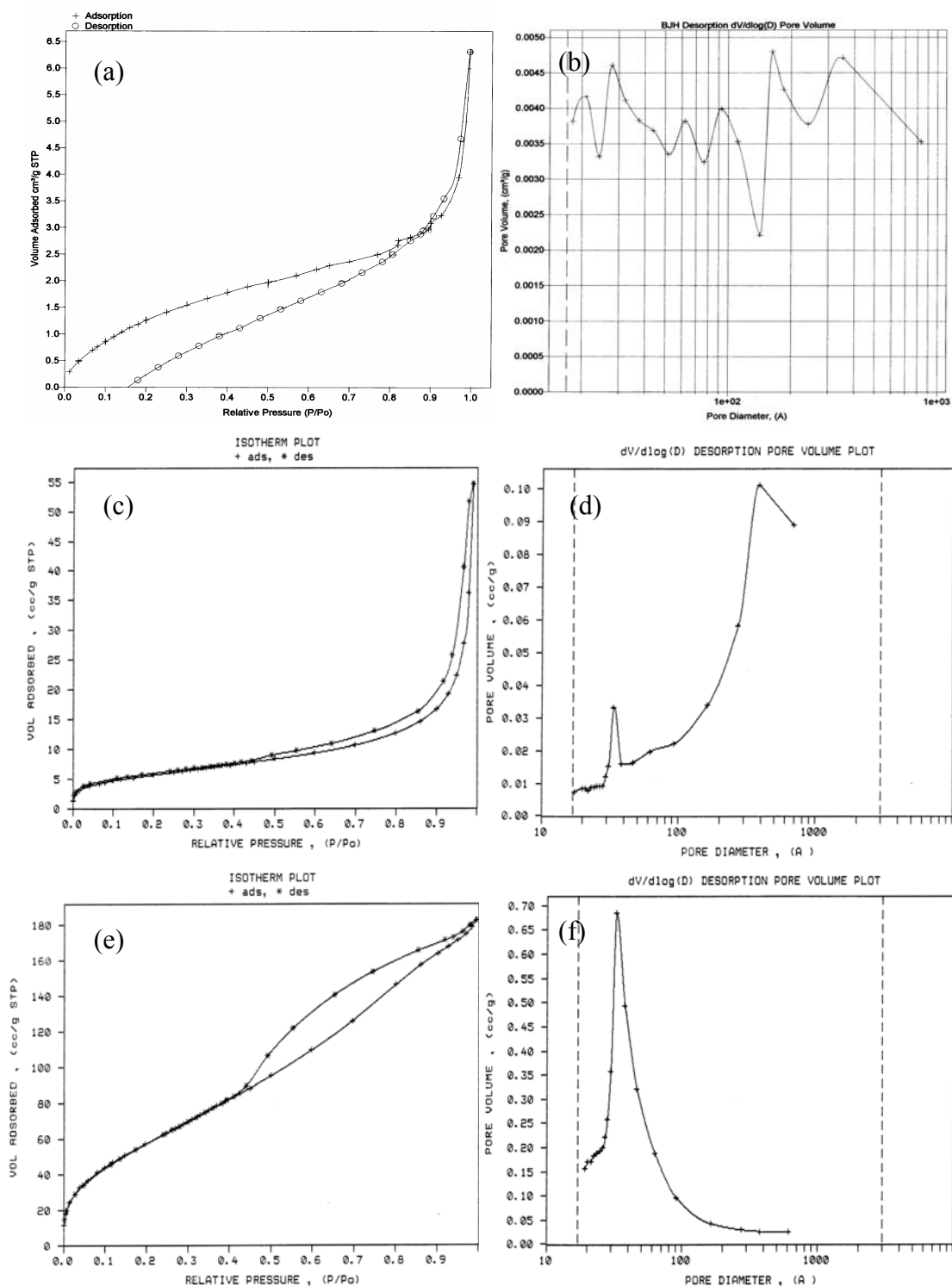
**Figure 4.7** Distribution of weight loss percentage against temperature stage for modified-PS-DVB resins

#### 4.4.4 Nitrogen Adsorption and Desorption Analysis

The nitrogen adsorption isotherm for product 2A is shown in Figure 4.8a. The nitrogen adsorption data of the product 1 resin was used as a reference to compare the types of pore, surface area and pore volume with the product 2A. As mentioned before in Figure 4.4a, the synthesized PS-DVB resin is not well formed. Based on the result, the synthesized PS-DVB resin contains a mixture of a narrow and wide mesopore. Figure 4.8a shows the nitrogen isotherm obtained from product 2A is not well formed. Therefore, the type of pores in the product 2A was a mixture of mesopore and macropore. This result suggests that the product 2A did not affect much on the surface properties of the studied phase.

The pore size distribution of the product 2A is shown in Figure 4.8b. It was found that the distribution of pore size for the product 2A was covered in the range of 20-700 Å. This result suggests the presence of different sizes of mesopore and macropore in the product 2A. In the present work, the distribution of pores for the synthesized PS-DVB resin was covered in the range of 20-40 Å (Figure 4.8d). The distribution of pores size for synthesized PS-DVB resin changed probably due to the effect of the Friedel Crafts acylation reaction.

All of the obtained data from nitrogen adsorption for modified-PS-DVB resin are summarized in Table 4.10. The data show that the product 2A has BET surface area of  $5.8 \text{ m}^2 \text{ g}^{-1}$  and average pore volume of  $9.8 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ . It was found that product 2A exhibits the higher BET surface area and average pore volume compared to the synthesized PS-DVB resin (Table 4.10). This result suggests that the product 2A increases the BET surface area and average pore volume of native PS-DVB. This can be proven with the significance change in the BET surface area and average pore volume of the synthesized PS-DVB resin after modification with acetyl chloride during the Friedel Crafts acylation reaction.



**Figure 4.8** (a) Nitrogen adsorption isotherm and (b) average pore size distribution of the product 2A; (c) Nitrogen adsorption isotherm and (d) average pore size distribution of the product 2B; (e) Nitrogen adsorption isotherm and (f) average pore size distribution of the product 2C

The adsorption/desorption isotherm of the product 2B (Figure 4.8c) was a type IV isotherm with a type H<sub>3</sub> hysteresis loop indicating the presence of slit-shaped pores. The presence of the loop in the high relative pressure region shows that the material is essentially mesoporous, with a minimal macropore contribution. The pore shape of the product 2B was clearly different from that of the synthesized PS-DVB resin and the product 2A.

The pore size distribution of the product 2B is shown in Figure 4.8d. It was found that the distribution of pores for the product 2B was covered in the range of 30-1000 Å. This result suggests that the presence of different sizes of mesopore and small amount of macropore in the product 2B. It is also recognized that the product 2B was distributed in wide range of mesopore compared to the product 2A. In the present work, the distribution of pores for the product 2A resin was covered in the range of 20.0-700.0 Å (Figure 4.8b).

**Table 4.10:** Pore and surface characteristic of modified-PS-DVB resin

Resin	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore width (Å)	Type of pore
Product 2A	5.8	$9.8 \times 10^{-3}$	67.9	Meso & macro
Product 2B	20.2	$5.6 \times 10^{-2}$	110.9	Meso & macro
Product 2C	227.8	$2.8 \times 10^{-1}$	48.5	Meso

The product 2C had type IV isotherm with an intermediate type H<sub>3</sub>-H<sub>2</sub> hysteresis loop. This isotherm is depicted in Figure 4.8e. The type IV isotherm is associated with a material containing mesopores. The type H<sub>2</sub> hysteresis loop is a typical of inorganic oxides and usually indicates that the adsorbent contains a wide pore size distribution with pores containing wide bodies and narrow necks, the so-called ‘ink bottle’ shape pores. A type H<sub>3</sub> hysteresis loop is usually associated with the material that has been formed from the agglomeration of small spheres in a

regular array yielding a uniform and narrow pore size distribution.

The resulting pores are usually consisting of slit shape pore. A hysteresis loop intermediate between  $H_2$  and  $H_3$  indicates a combination of the two types of pores, i.e. ‘ink bottle’ shaped pores and slit shaped pores. The change in shape of the hysteresis loop for the product 2B to the product 2C from a type  $H_3$  to a type  $H_2$  indicates that the process of particle sintering and crystallization started to build the necks of the narrow pores.

From Figure 4.8f, it was found that the distribution of the pores for product 2C resin was covered in the range of 30.0-70.0 Å. These suggest that only mesopore present in the product 2C. The data obtained from nitrogen gas adsorption (Table 4.10), the product 2C has the BET surface area of  $227.8 \text{ m}^2 \text{ g}^{-1}$ , average pore volume of  $2.8 \times 10^{-1} \text{ cm}^3 \text{ g}^{-1}$  and average pore diameter of 48.5 Å. The results in Table 4.10 illustrate that the BET surface areas increase as the modified steps started from the product 2A resin followed by the product 2C. As expected, the BET surface area of product 2A is greater than the synthesized PS-DVB resin probably due to the presence of product 2A during the modification process. It is also recognized that the BET surface area of the product 2B increased may be due to the Grignard agent (methyl magnesium chloride) during the Grignard reaction.

In other words, it can be proven that the product 2A, product 2B and product 2C show a significance change in the BET surface area, average pore volume and average pore diameter after modification with zirconia. The properties changed probably because of the effect of heat during the Friedel Crafts acylation and Grignard reactions. It also probably affected by the presence of zirconia oxide in the resins during the modification process of PS-DVB resin. Therefore, it could be concluded that the modification of synthesized PS-DVB resin with zirconyl chloride did significantly affect the surface properties of the sample.

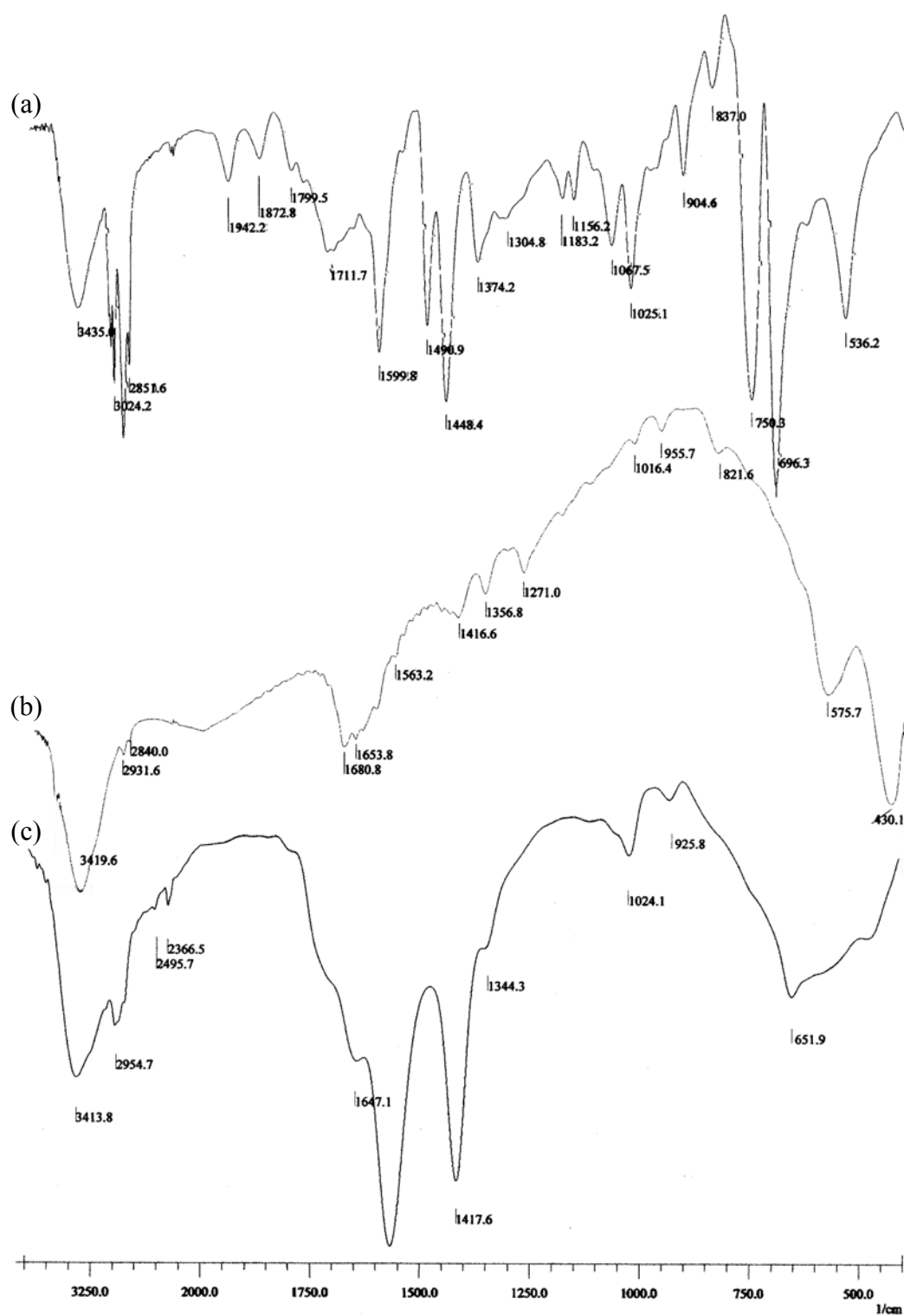
#### 4.5 Preparation of *p*-2-zirconyl-2-methylpropyl-PS-DVB chloride

The polymer adsorbent of *p*-2-zirconyl-2-methylpropyl-PS-DVB chloride resin was prepared using three steps polymer analogous reaction. It was coded as product 3C. At first, a ketone group  $\text{CH}_3\text{-COCH}_2\text{-}$  was introduced into the synthesized PS-DVB using Friedel Crafts acylation reaction with chloroacetone with the presence of  $\text{AlCl}_3$  as Lewis acid catalyst. The ketone functional resin showed an intense carbonyl stretching at  $1711.7\text{ cm}^{-1}$  in the FTIR spectrum. It produced *p*-2-propanoyl-PS-DVB and coded as product 3A. *p*-2-propanoyl-PS-DVB was then converted to product 3B (*p*-2-hydroxyl-2-methylpropyl-PS-DVB) using Grignard reaction with methyl magnesium chloride, followed by hydrolysis. The *p*-2-hydroxyl-2-methylpropyl-PS-DVB was allowed to react with zirconyl chloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) in acetonitrile-water (1:1) mixture to afford the polymer *p*-2-zirconyl-2-methylpropyl-PS-DVB chloride. The reaction sequence is depicted in Figure 1.1c.

#### 4.6 Characterization of *p*-2-zirconyl-2-methylpropyl-PS-DVB chloride

##### 4.6.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analysis of product 3A in Figure 4.9a shows its peaks at  $3000.2\text{ cm}^{-1}$  and  $3024.2\text{ cm}^{-1}$  which are assigned to  $\text{C-H}_{\text{alkanes}}$  and  $\text{C-H}_{\text{aromatic}}$  stretching, respectively. Polystyrene functional group shows its stretching absorbance at  $1942.2\text{ cm}^{-1}$ ,  $1872.8\text{ cm}^{-1}$ ,  $1799.5\text{ cm}^{-1}$  and  $1775.3\text{ cm}^{-1}$ . The  $\text{C}=\text{C}_{\text{aromatic}}$  stretching were absorbed at  $1599.8\text{ cm}^{-1}$  and  $1490.9\text{ cm}^{-1}$ . The presence of a  $\text{C}=\text{O}$  functional group in the modified phase is proven by a strong band at  $1711.7\text{ cm}^{-1}$  on spectrum. The para- and mono-substituted benzene rings were observed at  $750.3\text{ cm}^{-1}$  and  $696.3\text{ cm}^{-1}$ ,  $536.2\text{ cm}^{-1}$  respectively.



**Figure 4.9** FTIR spectra (a) product 3A, (b) product 3B and (c) product 3C

The absorption pattern of acetyl resin FTIR spectrum (Figure 4.9a) was identical to synthesized PS-DVB resin FTIR spectrum (Figure 4.1a) and it showed a strong absorption at  $1711.7\text{ cm}^{-1}$ , which indicate the existence of  $\text{C}=\text{O}_{\text{stretching}}$ . It means that the modification of synthesized PS-DVB resin with chloroacetone is successfully achieved. The FTIR spectrum showed that there was a similarity in the absorbed frequencies between synthesized PS-DVB resin and product 3A.

The FTIR analysis of Product 3B in Figure 4.9b shows its peaks at  $2931.6\text{ cm}^{-1}$  and  $2840.0\text{ cm}^{-1}$  which are assigned to  $\text{C}-\text{H}_{\text{alkanes}}$  stretching. The  $\text{C}=\text{C}_{\text{aromatic}}$  stretching is absorbed at  $1563.2\text{ cm}^{-1}$  and  $1416.6\text{ cm}^{-1}$ . The presence of the  $-\text{OH}$  functional group in the modified phase is proven by a strong band at  $3419.6\text{ cm}^{-1}$  on spectrum. The para- and mono-substituted benzene rings were observed at  $575.7\text{ cm}^{-1}$  and  $430.1\text{ cm}^{-1}$ .

FTIR spectrum obtained from product 3C showed that the sample gave similar adsorption bands with product 3B except for the spectrum at product 3C exhibits an extra broad band may be attributed to the stretching vibration of the  $-\text{OH}$  group present in the sample. Table 4.11 summarizes the FTIR absorption data incorporating functional groups from the FTIR spectra of PS-DVB-modified resin.

**Table 4.11:** Absorbance signals for the functional groups modification PS-DVB using chloroacetone

Functional Groups	Resin		
	Product 3A	Product 3B	Product 3C
	Wave number, $\text{cm}^{-1}$		
OH	3435.0 ( <i>l</i> )	3419.6 ( <i>h</i> )	3413.8 ( <i>h</i> )
$=\text{C}-\text{H}_{\text{aromatic}}$	3024.2	-	-
$-\text{CH}_{\text{saturated}}$	3000.2, 2851.6	2931.6, 2840.0	2954.7
$\text{C}=\text{O}$	1711.7	1680.8	-
$\text{C}=\text{C}_{\text{aromatic}}$	1599.8, 1490.9	1563.2, 1416.6	1575.5



#### 4.6.2 Scanning Electron Microscopy Analysis

The product 3A resin shows significant changes in their physical properties, compared to the synthesized PS-DVB resin (Figure 4.10a). The chemical or physical interaction may occur between chloroacetone and synthesized PS-DVB resin during the Friedel Crafts acylation reaction. It is probably due to the reaction condition in the reaction. The product 3A particles fused into large units, known as aggregates and eventually these aggregates flocculate to form agglomerates.

In addition, the morphology of the particles formed showed that they are relatively irregular, poly-disperse and split neatly into several groups. In the case of the surface of particles (Figure 4.10b), after 5000 $\times$  of magnification the surface of the acetone resin particles looks like a sticky surface and similarly coated by a new layer. It is probably an effect from the heating process during the Friedel Crafts acylation reaction. From this figure, it can be expected that the change of surface morphology has occurred from homogeneous surface of the PS-DVB resin to heterogeneous surface of the product 3A and it clearly shows the formation of some cracks on the surface.

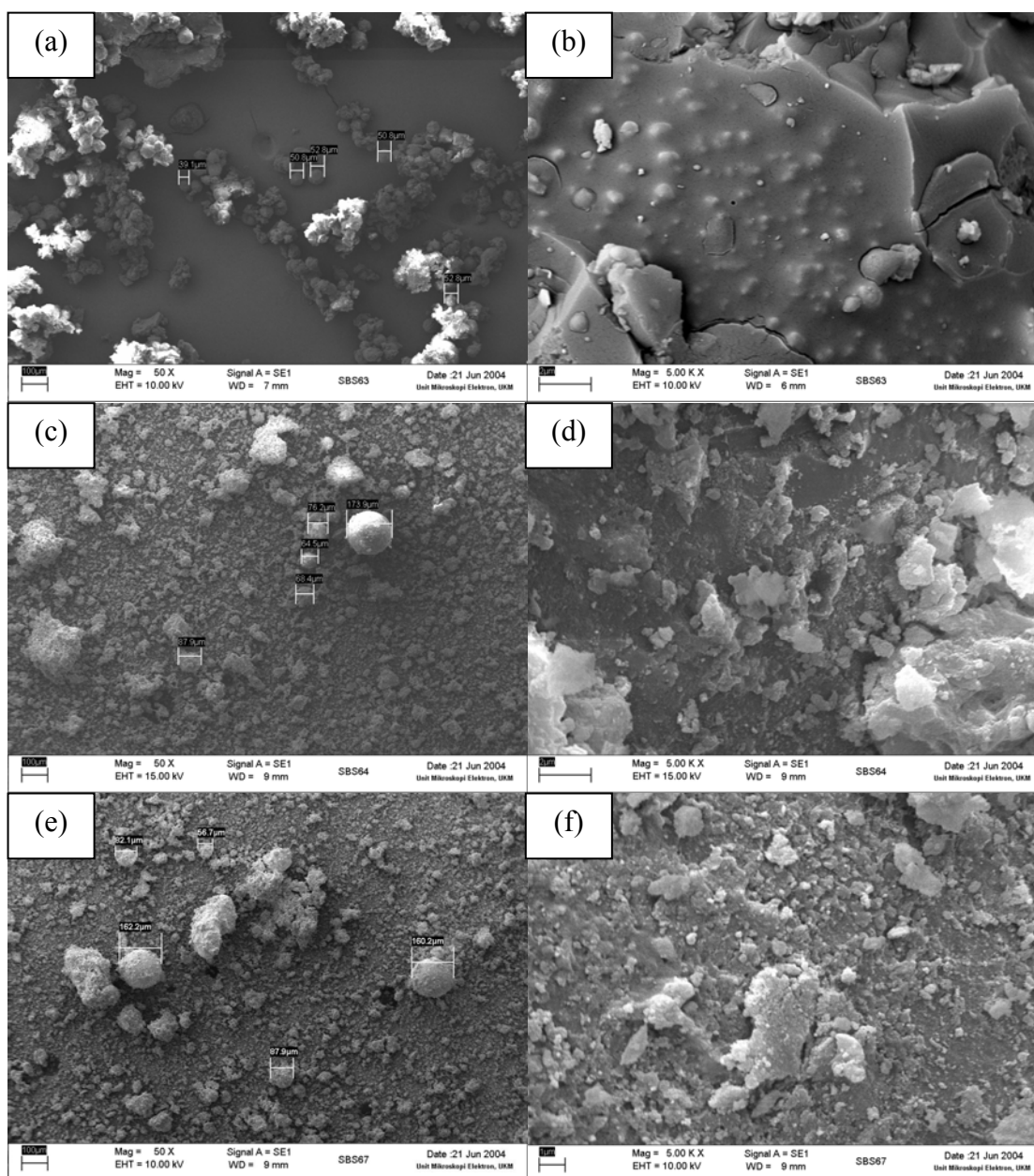
Product 3B was also characterized using SEM and it was noticed that substantial enlargement occurred while preparing the sample. A typical scanning electron micrograph for this solid is shown in Figure 4.10c and corresponds to the condition of the material after Grignard reaction process. This particular micrograph illustrates the irregular nature of the solid as initially prepared and supports the view that it is in different size mono-disperse. A spherical morphology was also observed, although in this case some debris appeared on the particle. The morphology similar to that shown in Product 3B (Figure 4.10c) was observed. The new layer on the particle was also clearly recognizable but, as in the previous explanation, it was not possible to determine the thickness.

The morphology of the surface of product 3B is irregular (Figure 4.10d). The surface properties were altered due to the presence of the agent of methyl magnesium chloride or thorough refluxing process in Grignard reaction. From Figure 4.10, it was

found that the particle size for product 3A, product 3B and product 3C were about 85.2, 94.2 and 109.8  $\mu\text{m}$ , respectively. This result reflects that the particle size of the modified-PS-DVB resin is dramatically increased by the modification process steps of the synthesized PS-DVB resin.

In the micrograph of product 3C particles (Figure 4.10e), morphology similar to that shown in product 3C (Figure 4.6e). These observations indirectly imply that a reflux process change the morphology of Product 3B to Product 3C, which alter the mechanical properties. The arrangement of the particle is random and does not show any specific pattern. The morphology of the particles formed showed that they are irregular. However, the morphology of the surface of Product 3C does not show any specific pattern (Figure 4.10f). Thus, it is suggested that the mixing process interrupted the relatively ordered arrangement of multiplets, resulting in scattering centers of various scattering intensities at varying distances. This formation is supportive for the morphological changes upon blending in the present work (Coutinho *et al.*, 2004).

Based on these initial experiments we propose that it could be due to the difference in viscosity of the two kinds of composite during the polymerization process. Low energy sites are probably formed around all the surface of the high viscosity beads and facilitate the sorption of the iron particles. On the other hand, only few sites of low energy could be observed on the surface of the low viscosity ones. In this case, the particles seemingly prefer to form in clusters arrangement instead of nucleating (Coutinho *et al.*, 2004; Maria *et al.*, 2003a and 2003b; Huang and Tang, 2004).



**Figure 4.10** SEM micrographs of modification PS-DVB using chloroacetone: (a) product 3A; magnification 50 $\times$  and (b) magnification 5000 $\times$  (c) product 3B; magnification 50 $\times$  and (d) magnification 5000 $\times$  (e) product 3C; magnification 50 $\times$  and (f) magnification 5000 $\times$

#### 4.6.3 Thermogravimetry Analysis

The thermogravimetric analysis result for modified-PS-DVB resin at various temperature ranges are listed in Table 4.12. Temperature range less than 135.5°C and temperature range 135.5-326.6°C show that the Product 3B (19.0%) and Product 3A (24.8%) are the highest weight loss percentage compared to the other resins, respectively. These results reflect that the loss in weight observed at the temperature range less than 135.5°C is probably due to the removal of the loosely bound water from the resin while the loss in weight at temperature range 135.5-326.6°C corresponds to the removal of more strongly bounded water derived from hydroxyl groups and may also due to the decomposition of low volatile groups. The result indicates that the both resin may have a high degree of water contained in their structure compared to the other resins.

Table 4.12 also indicates that the maximum weight loss for most of the sample occurred at temperature range 326.6-517.6°C except for Product 3A, which occurs at temperature range of 517.6-708.6°C. The maximum weight loss percentage for Product 3A, Product 3B, and Product 3C are observed at temperature range of 517.6-708.6°C (32.98%), temperature range 326.6-517.6°C (22.5%), and temperature range 326.6-517.6°C (23.1%), respectively. Meanwhile, the weight lost occurred at temperature range 326.6-517.6°C, 517.6-708.6°C and 708.6-899.7°C arises from further decomposition of the high volatile groups in the resin. The result demonstrates that the maximum weight loss percentage of the resins in Table 4.12 in accordance as Product 3A < Product 3B < Product 3C.

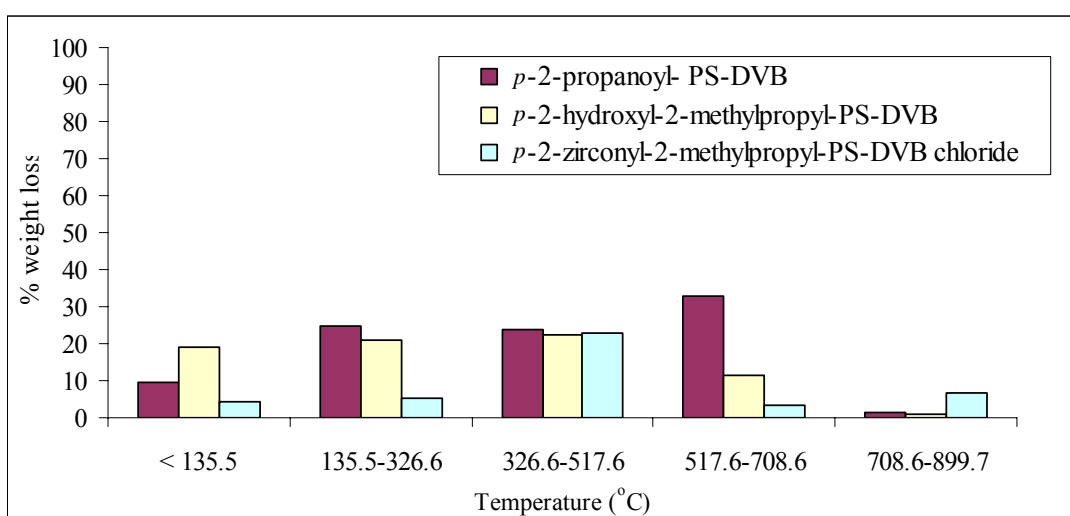
The residue percentage for Product 3A, Product 3B and Product 3C when the temperature reaches 900°C are 7.4%, 25.1%, and 57.7%, respectively. The percentage of residue of Product 3C is higher (57.7%) than the other resins. The total value of the percentage of weight loss of Product 3C is 42.4%. This result is probably affected by the presence of zirconia oxide in the resin during the modification process of PS-DVB resin. The properties changed probably because of the effect of heat during the Friedel Crafts acylation and Grignard reactions. The result

demonstrates that the arrangement of the thermal stability of the resins in Table 4.12 in accordance as product 3A < product 3B < product 3C.

**Table 4.12:** Thermogravimetric analysis results of modified PS-DVB using chloroacetone at various temperature ranges

Resin	% weight loss					Residue (%)
	< 135.5	135.5-326.6	326.6-517.6	517.6-708.6	708.6-899.7	
Product 3A	9.4	24.8	23.9	33.0	1.5	7.4
Product 3B	19.0	21.1	22.5	11.2	1.2	25.1
Product 3C	4.1	5.1	23.1	3.3	6.7	57.7

Figure 4.11 shows the graph of weight loss percentage of modification PS-DVB using chloroacetone (product 3A, product 3B and product 3C) against various temperature stages. The graph presents the percentage of weight loss for all resins that show a similar thermal stability distribution pattern. At the temperature stage 517.6-708.6°C the weight loss percentage has increased probably due to the decomposition of the most volatile organic compounds exist in the resins. At this stage, it shows that the weight loss percentage of acetone resin is the highest (33.0%). The results indicate that at temperature range 326.6-517.6°C, the modified resins are more stable than unmodified resins (Section 4.2.3). The results are probably affected by the chloroacetone reagents in the Friedel Crafts acylation.



**Figure 4.11** Graph of weight loss percentage against temperature stage for modified-PS-DVB resins

#### 4.6.4 Nitrogen Adsorption and Desorption Analysis

The nitrogen adsorption isotherm for product 3A is shown in Figure 4.12a. The nitrogen adsorption and desorption isotherms for product 3A and synthesized PS-DVB resin (Figure 4.4a) have a similar pattern, with low BET surface area. Figure 4.12a shows the nitrogen isotherm obtained from acetone resin was not well formed. Therefore, the type of pores in the acetone resin was a mixture of mesopore and macropore (Figure 4.12b). This result suggested that the acetone resin did not affect much on the surface properties of the studied phase.

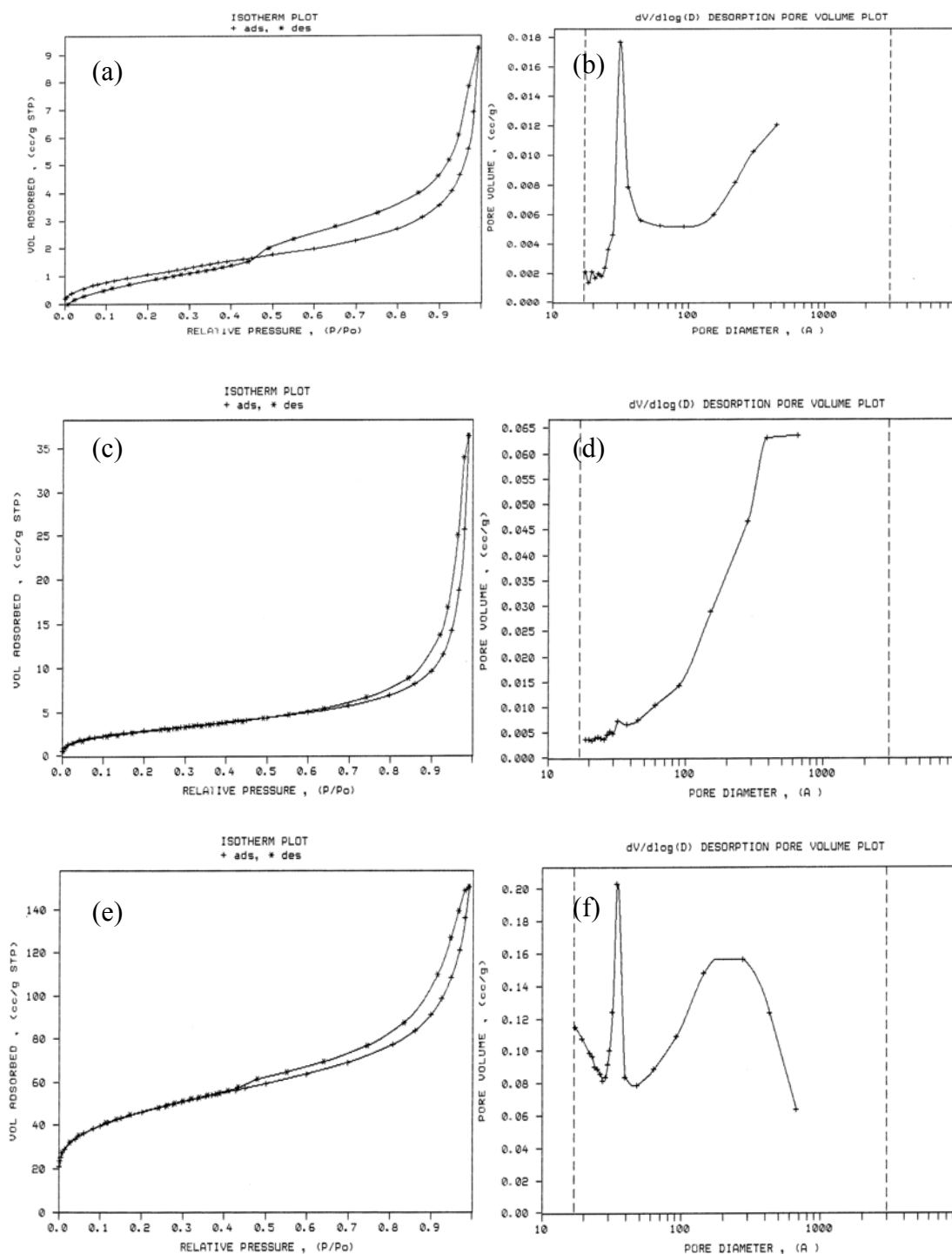
The pore size distribution of the product 3A is shown in Figure 4.12b. It was found that the distribution of pore size for the product 3A resin was covered in the range of 20.0-700.0 Å. This result suggests the presence of different sizes of mesopore and macropore in the product 3A. In the present work, the distribution of pores size for the synthesized PS-DVB resin was covered in the range of 20.0-40.0 Å (Figure 4.12d). From the results, it can be mentioned that the distribution of pores size for synthesized PS-DVB resin was changed probably due to the effect of the Friedel Crafts acylation reaction or the presence of chloroacetone reagent. The adsorption/desorption isotherm of the product 3B (Figure 4.12c) was a type IV isotherm with a type H<sub>3</sub> hysteresis loop indicating the presence of slit-shaped pores. The presence of the loop in the high relative pressure region shows that the material is essentially mesoporous, with a minimal macropore contribution. Regarding the result, the pore shape of the product 3B was clearly different from the synthesized PS-DVB resin and the product 3C. The pore size distribution of the product 3B is shown in Figure 4.12d. It was found that the distribution of pores size for the product 3B was covered in the range of 300-1000 Å. This result suggests the presence a mixture of mesopore and minimal macropore consists in the product 3B. It is also recognized that the product 3B was distributed in the wide range of mesopore compared to the acetone resin. In the present work, the distribution of pores size for the acetone resin was covered in the range of 20.0-700.0 Å (Figure 4.12b).

The nitrogen isotherm of the product 3C was a type IV isotherm with a type H<sub>3</sub> hysteresis loop indicating the presence of slit-shaped pores. The type IV isotherm

is associated with a material containing mesopores. This isotherm is depicted in Figure 4.12e. The presence of the loop in the high relative pressure region shows that the material is essentially narrow and wide mesoporous. Regarding the result, the pore shape of the product 3B was clearly different from that of the synthesized PS-DVB resin and the product 3A. A type H<sub>3</sub> hysteresis loop is usually associated with material that has been formed from the agglomeration of small spheres in a regular array yielding a uniform and narrow pore size distribution. From Figure 4.12f, the product 3C was found that the distribution of the pores size was covered in the range of 30-700 Å. These suggest the presence of mixture narrow and wider mesoporous in the product 3C.

The nitrogen adsorption data of the synthesized PS-DVB resin (Table 4.4) was used as a reference to compare the types of pore, surface area and pore volume with the modified-PS-DVB resin (Table 4.13). The results in Table 4.16 illustrate that the BET surface areas increase as the modified steps started from the *p*-2-propanoyl-PS-DVB resin followed by the product 3C. As expected, the BET surface area of acetone resin is greater than the synthesized PS-DVB resin probably due to the presence of chloroacetone during the modification process.

It is also recognized that the BET surface area of the product 3B increased due to the Grignard agent (methyl magnesium chloride) during the Grignard reaction. In other words, it can prove that the product 3A, product 3B and product 3C show a significance change in the BET surface area, average pore volume and average pore diameter after modification with zirconia. The properties changed probably because of the effect of heat during the Friedel Crafts acylation and Grignard reactions. It also probably affected by the presence of zirconia oxide in the resin during the modification process of PS-DVB resin. Therefore, it could be concluded that the modification of synthesized PS-DVB resin with zirconyl chloride did significantly affect the surface properties of the sample.



**Figure 4.12** (a) Nitrogen adsorption isotherm and (b) average pore size distribution of the product 3A; (c) Nitrogen adsorption isotherm and (d) average pore size distribution of the product 3B; (e) Nitrogen adsorption isotherm and (f) average pore size distribution of the product 3C



**Table 4.13:** Pore and surface characteristic of PS-DVB-modified resin

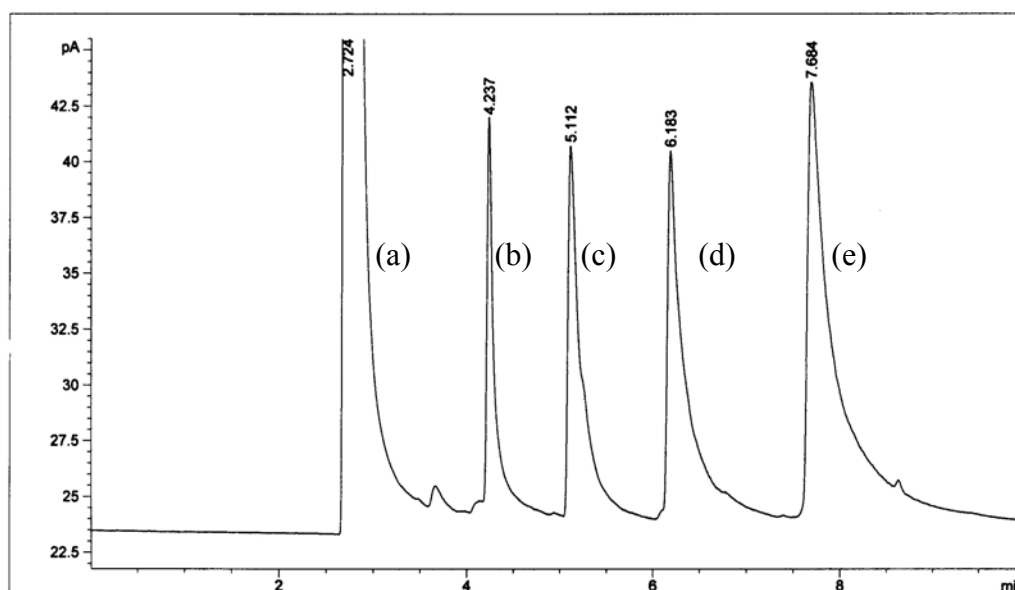
<b>Resin</b>	<b>BET surface area (m<sup>2</sup>g<sup>-1</sup>)</b>	<b>Total pore volume (cm<sup>3</sup>g<sup>-1</sup>)</b>	<b>Average pore width (Å)</b>	<b>Type of pore</b>
Product 3A	4.4	$1.1 \times 10^{-2}$	97.2	Meso
Product 3B	10.5	$4.0 \times 10^{-2}$	151.5	Meso
Product 3C	150.1	$2.1 \times 10^{-1}$	32.0	Meso

#### 4.7 Application of PS-DVB and Modified PS-DVB in Solid Phase Extraction

In this research, solid phase extraction (SPE) has been carried out to observe the adsorption properties of the synthesized PS-DVB and modified PS-DVB adsorbents. The synthesized and modified PS-DVB adsorbents were compacted into separate SPE columns which were then tested for the separation of several test compounds. The efficiency of the resins in the SPE analysis is determined through comparison of the recovery percentage of the test compound from aqueous solution. The SPE analysis results for the different types of modified PS-DVB resins were compared.

##### 4.7.1 Retention Times and Response Factors of Analytes

A solution containing the four test compounds: 2-chlorophenol, nitrobenzene and propiophenone, and internal standard butyrophenone were injected into the GC-FID. The chromatogram obtained (Figure 4.13) show that the compounds were well separated. The peaks were identified based on the comparison of retention time with those obtained for individual injection of the compounds.



**Figure 4.13** Gas chromatogram of the separation of test compounds. Peaks: (a) methanol, (b) 2-chlorophenol, (c) nitrobenzene, (d) propiophenone, and (e) butyrophenone. Chromatographic condition : Ultra-1 column 932530 (30 m  $\times$  250  $\mu\text{m}$   $\times$  0.20  $\mu\text{m}$ ), Carrier gas: Helium; flow rate: 1.1 mL min<sup>-1</sup>; pressure: 75 kpa; detector: FID; injector temperature: 250°C; detector temperature: 310°C; initial temperature: 100°C with a hold time of 2 min; final temperature: 140°C, linear temperature programmed at 5°C min<sup>-1</sup> rise.

The elution order under the chromatographia condition is methanol (2.7 min), 2-chlorophenol (4.2 min), nitrobenzene (5.1 min), propiophenone (6.2 min) and butyrophenone (7.7 min). The peak area for the compounds was used to calculate the response factor ( $F$ ). The GC-FID analysis for each compounds were carried out in triplicate to determine the reproducibility of the analysis. Table 4.14 shows the response factors for the test compounds and internal standard.

**Table 4.14:** Retention times and response factors ( $F$ ) of the solvent, test compounds and internal standard

Analytes	Retention Time (min)	Response Factors ( $F$ )
Methanol	2.7	-
2-chlorophenol	4.2	$3.5 \times 10^{-2}$
Nitrobenzene	5.1	$3.5 \times 10^{-2}$
Propiophenone	6.2	$4.9 \times 10^{-2}$
Butyrophenone	7.7	$5.2 \times 10^{-2}$

## 4.8 Effect of eluant

In order to observe the influence of eluant towards the percentage recovery for each test compound. Three organic eluant were used, namely, methanol, acetonitrile and ethyl acetate. Percentage recovery for analytes is shown in Table 4.15. The results indicate that PS-DVB resin, product 2A, and product 3A give higher percentage recovery for 2-chlorophenol, nitrobenzene and propiophenone when methanol was used as elution solvent. However, the result for product 2B, product 3B, product 2C and product 3C exhibited higher recovery percentages for all test compounds when ethyl acetate was used as eluant. It was found that the SPE column packed with PS-DVB resin was less efficient with recoveries between 9.1%-63.4% with the ethyl acetate as eluant. The adsorption interaction between PS-DVB sorbent with test compounds is based on Van der-Waals interactions between the hydrophobic parts of the molecule with the non-polar matrix and  $\pi$ - $\pi$  interactions between the benzene ring of sorbent with the test compounds.

### 4.8.1 Methanol as eluant

The results of the percentage recovery of the test compound with methanol as the solution solvent for the PS-DVB resin and modified PS-DVB are given in Figure 4.14. This shows that a methanol is a better eluant for polar compounds which will retain in the PS-DVB resin, product 2A and product 3A such as nitrobenzene and propiophenone. This is due to the hydroxyl group in the methanol that can increase the dilution energy for analyte in PS-DVB resin, product 2A and product 3A.

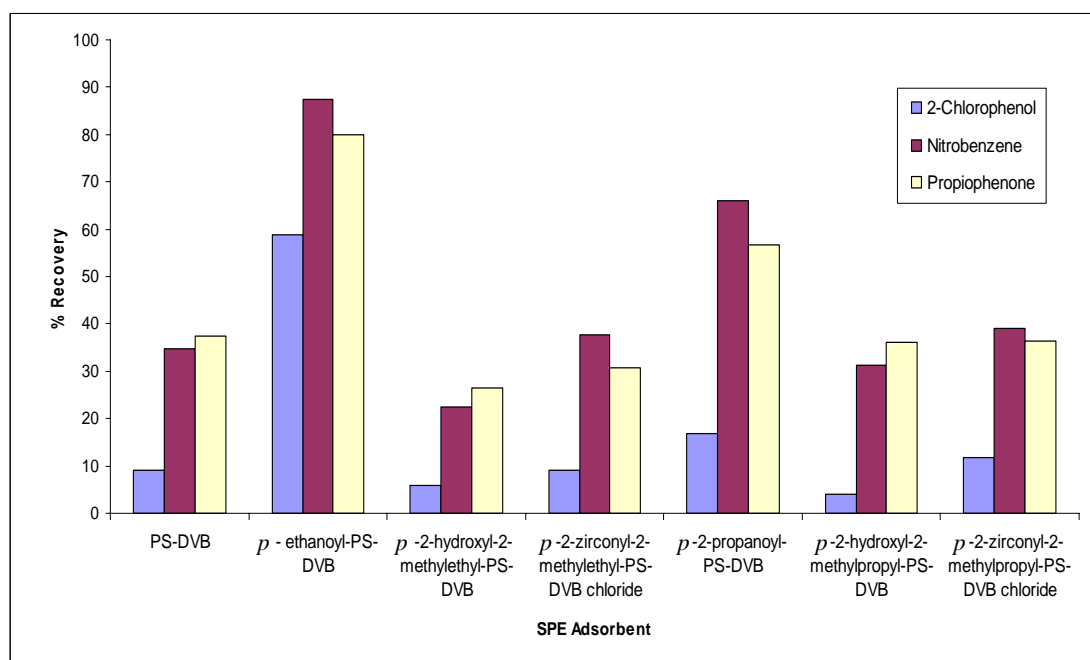
**Table 4.15:** Percentage recovery of analytes way methanol, acetonitrile and ethyl acetate as eluant for different adsorbents: synthesized PS-DVB, product 2A, product 3A, product 2B, product 3B, product 2C and product 3C

Eluant	Adsorbent						
	PS-DVB	Product 2A	Product 3A	Product 2B	Product 3B	Product 2C	Product 3C
Recovery (%)							
2-Chlorophenol							
Methanol	9.1 (1.3)	58.7 (5.0)	17.0 (3.2)	5.8 (2.6)	3.9 (0.5)	9.0 (1.4)	11.8 (0.3)
Acetonitrile	16.2 (13.5)	29.9 (2.9)	16.1 (1.2)	5.9 (1.4)	4.1 (1.9)	13.1 (1.9)	10.9 (4.4)
Ethyl Acetate	24.9 (7.2)	19.4 (4.0)	8.5 (0.9)	17.9 (2.2)	13.4 (1.4)	18.9 (0.5)	24.4 (0.4)
Nitrobenzene							
Methanol	34.6 (2.4)	87.3 (0.8)	66.1 (1.9)	22.4 (0.7)	31.3 (6.4)	37.7 (7.6)	39.1 (1.4)
Acetonitrile	63.4 (5.6)	37.6 (3.6)	35.7 (1.2)	21.0 (1.5)	31.2 (1.2)	38.4 (1.0)	36.9 (1.8)
Ethyl Acetate	20.7 (10.3)	15.8 (9.2)	23.2 (4.3)	46.1 (1.0)	51.3 (0.2)	41.9 (0.2)	48.3 (0.6)
Propiophenone							
Methanol	37.3 (1.1)	79.8 (0.5)	56.6 (2.1)	26.5 (0.6)	36.2 (1.3)	30.8 (0.3)	36.3 (0.3)
Acetonitrile	36.6 (5.5)	34.0 (4.1)	33.05 (1.45)	16.0 (0.5)	27.6 (1.5)	32.3 (0.5)	35.2 (1.9)
Ethyl Acetate	14.6 (3.9)	11.0 (1.9)	53.5 (1.9)	37.8 (1.1)	45.7 (0.3)	36.4 (0.2)	45.4 (0.4)

\* ( ) RSD base on nine injections

The results show that product 2A gives a high recovery percentage for nitrobenzene, 2-chlorophenol and propiophenone compared to other resins. This may be caused by the presence of carbonyl groups in the product 2A that can elevate the adsorption rate during the extraction process. However, the position of the carbonyl group in the resin structure also gives a slight influence to the adsorption rate. This can be proven by the ability of the *p*-2-propanoyl-PS-DVB to adsorb 30% less of test

compound compared to the product 2A. The position of the carbonyl groups which are directly bonded to the PS-DVB aromatic rings is expected have the ability to elevate the adsorption of the analytes. In contrast to the acetone resin, there are a number of  $-\text{CH}_2$  groups located in between the carbonyl groups and the aromatic rings.



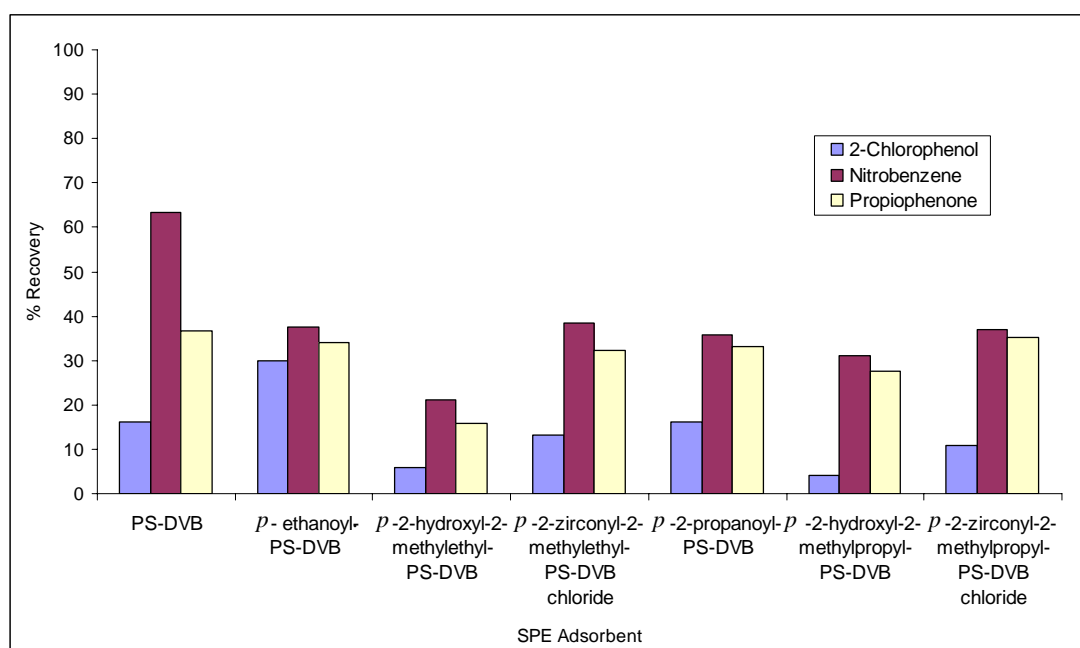
**Figure 4.14** Percentage recoveries of analytes extracted through different types of SPE adsorbent using [methanol](#) as the eluant

The results in Figure 4.14 show that product 2A and product 3A give higher recovery percentages for each analyte compared to product 2B and product 3B, respectively. The recovery percentage of both of the resins share a similar pattern, where propiophenone has a higher percentage and 2-chlorophenol has a lower percentage compared to nitrobenzene. It is expected that the presence of the hydroxyl group in product 2B and product 3B has lowered the ability of the resins to adsorb the analytes in the methanol condition. However, the percentage recovery of propiophenone in the product 3B is 36.19% which is higher than the 26.5% recovery percentage of the product 2B (Figure 4.15). This may be caused by the position of the hydroxyl groups in the product 3B which is farther apart from the aromatic PS-

DVB rings. The result of this study also show an increase in the percentage recovery of nitrobenzene in product 2B and product 3B compared to product 2C and product 3C, respectively. This may be caused by the adsorbent character those changes from the hydroxyl group –OH of the zirconia group that is bonded to the aromatic ring.

#### 4.8.2 Acetonitrile as eluant

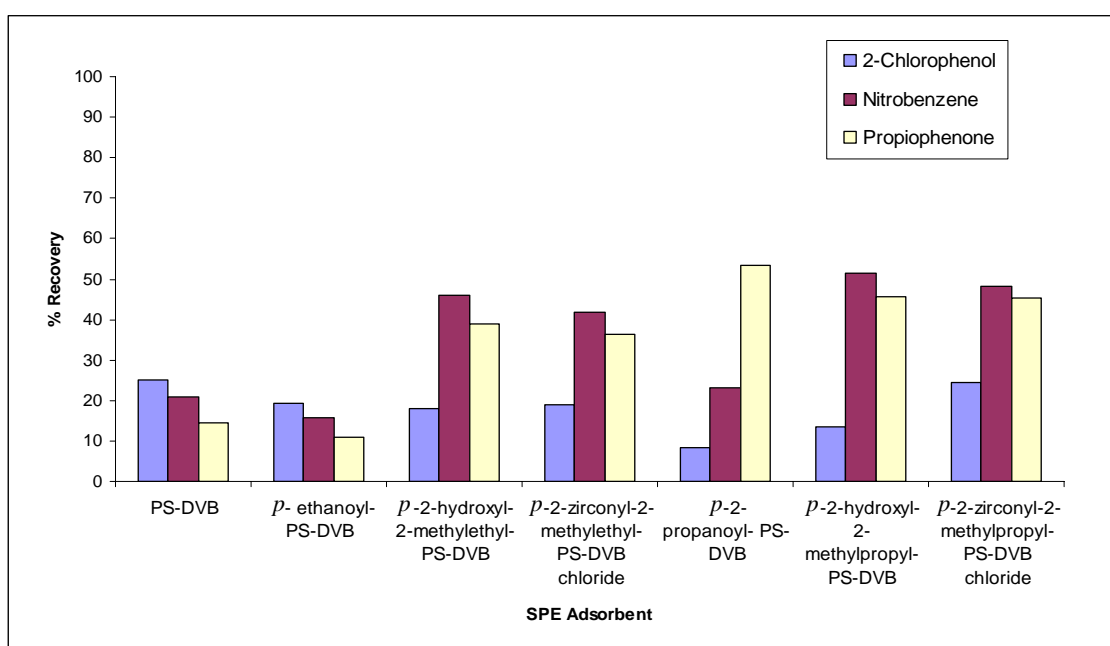
The results of the recovery percentage of the test compound with acetonitrile as the solvent for the PS-DVB resin and modified PS-DVB are shown in Figure 4.15. The results show that PS-DVB resin gives a high recovery percentage for nitrobenzene compared to other resins. However, the recovery percentages of propiophenone for all resins are similar. This may be caused by the effect of the some functional group in acetonitrile.



**Figure 4.15** Percentage recoveries of analytes extracted through different types of SPE columns using **acetonitrile** as the eluant

### 4.8.3 Ethyl acetate as eluant

Figure 4.16 shows the percentage recovery of the test compounds with ethyl acetate as the eluant for the PS-DVB resin and modified PS-DVB. The result shows an increase in the recovery percentage of nitrobenzene and propiophenone in modified PS-DVB compared to unmodified PS-DVB resin. It is expected due to the presence of some functional group in both resin and test compounds.



**Figure 4.16** Percentage recoveries of analytes extracted through different types of SPE columns using [ethyl acetate](#) as the eluant

## CHAPTER 5

### CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

#### 5.1 Conclusions

In this research, PS-DVB adsorbents have been successfully synthesized and subsequently modified. The effects of reaction time, stabilizer and polymerization method were investigated to determine suitable set of conditions to obtain PS-DVB resins with excellent physical properties. The optimum reaction time for polymerization was for 20.0 h at 70.0°C. The results showed that synthesized PS-DVB using poly(vinyl alcohol) as the stabilizer has the BET surface area of 1.2 m<sup>2</sup>/g and total pore volume of 1.2 × 10<sup>-3</sup> cm<sup>3</sup>/g and it is a better stabilizer than poly(vinyl pyrrolidone). The surfactant polymerization technique showed that the pore diameter (68.6 Å) of this sample is lower compared to the seeding polymerization technique.

Six different modified PS-DVB adsorbents namely, *p*-ethanoyl-PS-DVB, *p*-2-hydroxyl-2-methylethyl-PS-DVB, *p*-2-zirconyl-2-methylethyl-PS-DVB chloride, *p*-2-propanoyl-PS-DVB, *p*-2-hydroxyl-2-methylpropyl-PS-DVB, and *p*-2-zirconyl-2-methylpropyl-PS-DVB chloride have been completely characterized by using FTIR, SEM, TGA and Nitrogen adsorption.



This is evidence from the FTIR spectrum of synthesized PS-DVB resin that has similar adsorption pattern compared to the FTIR spectrum of commercial PS-DVB resin. For *p*-ethanoyl-PS-DVB and *p*-2-propanoyl-PS-DVB the presence of a C=O functional group in the modified phase was proven by strong band at 1678.9  $\text{cm}^{-1}$  and 1711.1  $\text{cm}^{-1}$ , respectively. This indicated the respective incorporation of the acetyl chloride and chloroacetone to the PS-DVB resin respectively.

In addition, the similarities between the spectra of *p*-ethanoyl-PS-DVB and *p*-2-propanoyl-PS-DVB indicate that the basic structural units of synthesized PS-DVB resin are preserved in the polymers. The FTIR analysis of *p*-2-hydroxyl-2-methylethyl-PS-DVB and *p*-2-hydroxyl-2-methylpropyl-PS-DVB show strong absorbent bands at 3430.1  $\text{cm}^{-1}$  and 3419.6  $\text{cm}^{-1}$ , respectively, which are assigned to the presence of -OH functional group in the modified phase. The scanning electron microscopy characterization, the micrograph showed that the synthesized PS-DVB resin exhibits somewhat uniform size and distributed in the wide range of particle size which is covered from 84.0-162.2  $\mu\text{m}$ .

In thermogravimetry analysis, the result represents the percentage weight loss for synthesized and commercial PS-DVB resins that show similar thermal stability distribution patterns where the percentage of weight loss at temperature stage less than 135.5°C and 135.5-326.6°C are lower than temperature stage of 326.6-517.6°C. The percentage weight loss has increased probably due to the decomposition of the most volatile organic compounds exist in the resins. This stage shows that the percentage weight loss of synthesized PS-DVB resin is slightly higher (73.5%) compared to the commercial PS-DVB resin (56.6%).

The result indicate that the synthesized PS-DVB resin have slightly higher BET surface area; average pore volume and average pore diameter compared than the commercial PS-DVB resin. In general, the modified PS-DVB resins were mesoporous. Therefore, it could be concluded that the modification of synthesized PS-DVB resin with zirconyl chloride did significantly affect the surface properties of the sample.

The GC-FID chromatogram shows that the earliest retention time of 2.7 min was referred to methanol, followed by 2-chlorophenol, nitrobenzene, propiophenone and lastly, butyrophenone, with the retention time at 4.2 min, 5.1 min, 6.2 min and 7.7 min, respectively. The GC-FID analysis was repeated three times for each sample to determine the average of peak area reproducibility of the analysis. The results show the peak areas and response factors for 2-chlorophenol, nitrobenzene, propiophenone and butyrophenone are  $3.5 \times 10^{-2}$ ,  $3.5 \times 10^{-2}$ ,  $4.9 \times 10^{-2}$  and  $5.2 \times 10^{-2}$ , respectively.

Three types of organic elution solvent are used which are methanol, acetonitrile and ethyl acetate in order to observe the influence of elution towards the recovery percentage for each test compound. It was also found that methanol is a good eluting solvent to elute polar analytes retained in *p*-ethanoyl-PS-DVB sorbent. It is because methanol consists –OH groups, which can increase the solubility of analytes during the elution step, therefore giving higher recoveries compare to extraction using other adsorbents.

The result shows that *p*-ethanoyl-PS-DVB gives a high recovery percentage for nitrobenzene, 2-chlorophenol and propiophenone compared to other resins. This may be caused by the presence of carbonyl groups in the acetyl resin and that can elevate the adsorption rate during the extraction process. However, the position of the carbonyl group in the resin structure also gives a slight influence to the adsorption rate. This can be proven by the ability of the *p*-2-propanoyl-PS-DVB to adsorb 30% less of test compound compared to the *p*-ethanoyl-PS-DVB. The position of the carbonyl groups which are directly bonded to the PS-DVB aromatic rings is expected to have the ability to elevate the adsorption of the analytes.

## 5.2 Suggestions for Further Study

SPE with chemically modified sorbents has been carried out in the off-line and on-line modes by León-González and Pérez-Arribas (2000). In this research, SPE was carried out in the off-line mode. So, further studies could be conducted to carry out SPE with modified and unmodified PS-DVB sorbents in the on-line mode. On-line procedures use an extraction sorbent in a pre-column. The methods, which combine SPE with HPLC, are the most frequently used, mainly to determine polar compounds in water. In the on-line procedures, there is no sample manipulation between preconcentration and analysis, so loss and contamination risks are avoided, and detection limits and reproducibility values may be better.

In this work, the performances of the modified and unmodified PS-DVB sorbents in home made SPE column were determined and compared. Further studies could be conducted for the analysis of breakthrough curves to determine the efficiency of these adsorbents. As described previously, the breakthrough volume or retention volume for a particular analyte is a good indication of the extraction ability of the adsorbents (Dumont and Fritz, 1995). It corresponds to the aqueous sample volume that can be percolated through the SPE column without any loss of the analyte. It also means that the whole amount of analyte percolated is trapped by the sorbent.

## REFERENCES

- Aiken, B., Hsu, W. P. and Matijevic, E. (1990). Preparation and properties of uniform mixed and coated colloidal particles. *J. Mater. Sci.* 25: 1886-1894.
- Allcock, H. R., Lampe, F. W. and Mark, J. E. (2003). *Contemporary Polymer Chemistry*. 3<sup>rd</sup> Edition. Pearson Prentice Hall: New Jersey. 61-72.
- Bacquet, M., Salunkhe, M., and Caze, C. (1992). Influence of chlorosulfonation on textural chemical parameters of styrene-divinylbenzene porous copolymers. *Reactive Polym.* 16: 61-69.
- Baiulescu, G. E. and Ilie, V. A. (1975). *Stationary Phases in Gas Chromatography*. Hungary: Pergamon Press. 113-116, 295.
- Blumenthal, B. H. (1958). *The chemical behavior of zirconium*. Van Nostrand: New York. 36-41.
- Buchmeiser M. R. (2001). New synthetic ways for the preparation of high-performance liquid chromatography supports. *J. Chromatogr. A*. 918: 233-236.
- Camel, V. (2003). Solid phase extraction of trace elements. Review. *Spectrochimica Acta Part B*. 58: 1177-1233.
- Chambers, T. K. and Fritz, J. S. (1998). Effect of polystyrene-divinyl benzene resin sulfonation on solute retention in high-performance liquid chromatography. *J. Chromatogr. A*. 797: 139-147.

- Clark, R. H. J. (1975). *The Chemistry of Titanium, Zirconium & Hafnium*. Great Britain: Pergamon Press, 419-420.
- Conder, J. R. and Young, C. L. (1979). *Physicochemical Measurement by Gas Chromatography*. 1<sup>st</sup> ed. Great Britain: John Willey & Sons Ltd. 6. 79-93.
- Coutinho, F. M. B., Souza, R. R. and Gomes, A. S. (2004). Synthesis, characterization and evaluation of sulfonic resins as catalysts. *Eur. Polym. J.* 40: 1525-1532.
- Dumont, P. J. and Fritz, J. S. (1995). Effect of Resin Sulfonation on the Retention of Polar Organic Compounds in Solid-Phase Extraction. *J. Chromatogr. A.* 691: 123-131.
- Durst, H. D. and Gokel, G. W. (1980). *Experimental Organic Chemistry*. McGraw-Hill Book Company: New York. 50-59.
- Dyson, R. W. (1987). *Specialty Polymers*. Blackie & Son, London. 21-23.
- Edward, D. I. (1970). *Chromatography: Principles and Techniques*. London: Butterworth & Co. (Publishers) Ltd. 1-2.
- Ensing, K., Berggren, C. and Majors, R. E. (2002). Selective sorbents for SPE based on molecularly imprinted polymers. *LC-GC Europe. Sample preparation perspectives*. 2-8.
- Fontanals, N., Galià M., Marce R. M. and Borrull F. (2004). Solid-phase extraction of polar compounds with a hydrophilic copolymeric sorbent. *J. Chromatogr. A.* 1030: 63-68.
- Fritz, J. S., Dumont, P. J. And Schmidt, L. W. (1995). Methods and materials for solid-phase extraction. *J. Chromatogr. A.* 691: 133-140.

- Gauthier, M. A., Luo, J., Calvet, D., Ni, C., Zhu, X. X., Garon, M. and Buschmann, M. D. (2004). Degree of crosslinking and mechanical properties of crosslinked poly(vinyl alcohol) beads for use in solid-phase organic synthesis. *Polym.* 45: 8201-8210.
- Glajeh, J. J., Kirkland, J. J. and Kohler, J. (1987). Effect of column degradation on the RP high performance liquid chromatographic separation of peptides and proteins. *J. Chromatogr.* 384: 81.
- Green, C. E. and Abraham, M. H. (2000). Investigation into the effects of temperature and stirring rate on the solid-phase extraction of diuron from water using a C<sub>18</sub> extraction disk. *J. Chromatogr. A.* 885: 41-49.
- Gregg, S. J. and Sing, K. S. W. (1982). *Adsorption, surface area and porosity*. 2<sup>nd</sup> ed. London: Academic Press. 1 – 39.
- Gurdeep, R. C. (1974). *Adsorption and phase rule*. 2<sup>nd</sup> ed. Subhash Bazar: Goel Publishing House. 1 – 14, 43 – 49.
- Hennion, M. (1999). Solid phase extraction: method development, sorbents and coupling with liquid chromatography. Review. *J. Chromatogr. A.* 856: 3-54.
- Hennion, M. (2000). Graphitized carbons for solid-phase extraction. Review. *J. Chromatogr. A.* 885: 73-95.
- Hosoya, K., Kishii, Y., Kimata, K., Araki, T., Tanaka, N., Svec, F. and Fréchet, J. M. J. (1995). Uniform-size hydrophobic polymer-based separation media selectively modified with a hydrophilic external polymeric layer. *J. Chromatogr. A.* 690: 21-28.
- Howdle, S. M., Jerábek, Leocorbo, V., Marr, P.C. and Sherrington, D.C. (2000). Reversibly collapsible macroporous poly(styrene-divinyl benzene) resins. *Polymer Communication.* 41: 7273-7277.

- Hu, Y. L., Feng, Y. Q., Wan, J. D. and Da, S. L. (2001). Native and Stearic Acid Modified Ceria-Zirconia Supports in Normal and Reversed-Phase HPLC. *Talanta*. 54: 79-88.
- Huang, Z. and Tang, F. (2004). Preparation, structure, and magnetic properties of polystyrene coated by Fe<sub>3</sub>O<sub>4</sub> nanoparticles. *J. Colloid Interface Science*. 275: 142-147.
- Huck, C. W. and Bonn, G. K. (2000). Recent developments in polymer-based sorbents for solid-phase extraction. Review. *J. Chromatogr. A*. 885: 51-72.
- Hussain, A. (1984). *Thermal and surface studies of the decomposition of the various zirconium compounds*. PhD Thesis. 64, 49-57.
- Klingenberg, A. and Seubert, A. (2002). Sulfoacylated poly(styrene-divinyl benzene) copolymers as resins for cation chromatography: comparison with sulfonated, dynamically coated and silica gel cation exchangers. *J. Chromatogr. A*. 946: 91-97.
- Knox, J. H., Unger, K. K. and Mueller, H. (1983). Prospects for Carbon as Packing Material in High Performance Liquid Chromatography. *J. Liq Chromatogr*. 6 (Suppl.) 1: 1-36.
- Legido-Quigley, C. and Smith, N. W. (2004a). Study of short polystyrene monolith-fritted micro-liquid chromatography columns for analysis of neutral and basic compounds. *J. Chromatogr. A*. 1042: 61-68.
- Legido-Quigley, C., Marlin, N. and Smith, N. W. (2004b). Comparison of styrene-divinylbenzene-based monoliths and Vydac nano-liquid chromatography columns for protein analysis. *J. Chromatogr. A*. 1030: 195-200.
- León-González, M. E. and Pérez-Arribas, L. V. (2000). Chemically modified polymeric sorbents for sample preconcentration. *J. Chromatogr. A*. 902: 3-16.

- Li, J., Litwinson, L. M. and Cantwell, F. F., (1996). Intra-particle sorption rate and liquid chromatographic bandbroadening in porous polymer packings II. Slow sorption rate on a microparticle packing. *J. Chromatogr. A.* 726: 25-36.
- Li, J., Reeder, D. H., McCormick, A. V. and Carr, P. W. (1997). Factors influencing polybutadiene deposition within porous chromatographic zirconia. *J. Chromatog. A.* 791: 45-52.
- Liska, I. (2000). Fifty years of SPE in water analysis-historical development and overview. Review. *J. Chromatogr. A.* 885: 3-16.
- Liu, Y. and Pietrzyk, D. J. (2001). Capillary-electrochromatographic separations with copolymeric reversed-stationary phase and ion-exchanger-packed columns. *J. Chromatogr. A.* 920: 367-375.
- Mahdavian, A. R. and Khoei, S. (2002). A facile and efficient method for preparation of chiral supported poly(styrene-divinyl benzene) copolymers. *Reactive & Func. Polym.* 50: 217-223.
- Malik, M. A., Ahmed, M. and Ikram, M. (2004). A new method to estimate pore volume of porous styrene-divinyl benzene copolymers. *Polym. Testing.* 23: 835-838.
- Marce, R. M. and Borrull, F. (2000). Solid-phase extraction of polycyclic aromatic compounds. Review. *J. Chromatogr. A.* 885: 273-290.
- Maria, L. C. S., Aguiar, M. R. M. P., Guimaraes, P. I. C., Amorim, M. C. V., Costa, M. A. S., Almeida, R. S. M., Aguiar, A. P. and Oliveira, A. J. B. (2003a). Synthesis of crosslinked resin based on methacrylamide, styrene and divinyl benzene obtained from polymerization in aqueous suspension. *Eur. Polym. J.* 39: 291-296.



- Maria, L. C. S., Leite, M. C. A. M., Costa, M. A.S., Ribeiro, J. M. S., Senna, L. F. and Silva, M. R. (2003b). Preparation of composite materials containing iron in a cross-linked resin host based on styrene and divinyl benzene. *Eur. Polym. J.* 39: 843-846.
- Martin, C., Ramirez, L. and Cuellar, J. (2003). Stainless steel microbeads coated with sulfonated polystyrene-co-divinyl benzene. *Surface & Coatings Technology*, 165: 58-64.
- Masqué, N., Galiá, M., Marcé, R. M. and Borrull, F. (1998). New chemically modified polymeric resin for solid-phase extraction of pesticides and phenolic compounds from water. *J. Chromatogr. A.* 803: 147-155.
- Matyjaszewski, K. and Davis, T. P. (1998). *Handbook of Radical Polymerization*. Wiley-Interscience. John Wiley & Sons, Inc. USA. 1-3, 302: 854-855.
- McNeff, C., Zigan, L., Johnson, K., Carr, P. W., Wang, A. and Weber-Main, A. M. (2000). Analytical advantages of highly stable stationary phases for reversed-phase LC, LC-GC, Vol 18: 5, 514-529.
- Melo, L. F. C., Collins, C. H. and Jardim, I. C. S. F. (2004). New materials for solid-phase extraction and multiclass high-performance liquid chromatographic analysis of pesticides in grapes. *J. Chromatogr. A.* 1032: 51-58.
- Nash, D. C. and Chase, H. A. (1998). Comparison of diffusion and diffusion-convection matrices for use in ion-exchange separations of proteins. *J. Chromatogr. A.* 807: 185-207.
- Nawrocki, J. Rigney, M. P., McCromick, A. and Carr, P. W. (1993). Chemistry of zirconia and its use in chromatography. *J. Chromatogr. A.* 657: 229-282.
- Nilsson, U. J. (2000). Solid-phase extraction for combinatorial libraries. Review. *J. Chromatogr. A.* 885: 305-319.

- Ohta, K., Ohashi, M., Jin, J. Y., Takeuchi, T., Fujimoto, C., Choi, S. H., Ryoo, J. J. and Lee, K. P. (2004). Retention behavior of C<sub>1</sub>-C<sub>6</sub> aliphatic monoamines on anion-exchange and polymethacrylate resins with heptylamine as eluent. *J. Chromatogr. A*. 1039: 179-186.
- Olah, G. A. (1973). *Friedel-Crafts Chemistry*. John Wiley & Sons: New York-London-Sydney-Toronto. 1-30, 91-95.
- Pico, Y., Font, G., Molto, J. C. and Manes, J. (2000). Solid-phase extraction of quaternary ammonium herbicides. Review. *J. Chromatogr. A*. 885: 251-271.
- Rigney, M. P., Funkenbush, E. F. and Carr, P. W. (1990). Physical and chemical characterization of microporous zirconia. *J. Chromatogr. A*. 499: 291-304.
- Rigney, M. P., Weber, T. P. and Carr, P. W. (1989). Preparation and Evaluation of a Polymer Coated Zirconia RP-Chromatographic Support. *J. Chromatogr.* 484: 273.
- Rodriguez, I., Llompart, M. P. and Cela, R., (2000). Solid-phase extraction of phenols. Review. *J. Chromatogr. A*. 885: 291-304.
- Sabik, H., Jeannot, R. and Rondeau, B. (2000). Multiresidue methods using solid-phase extraction techniques for monitoring priority pesticides, including triazines and degradation products, in ground and surface waters. Review. *J. Chromatogr. A*. 885: 217-236.
- Safarikova, M. and Safarik, I. (2002). Magnetic SPE of target analytes from large volumes of urine. *Eur cells and materials*. Vol. 3, Suppl. 2: 192-195.
- Sandler, S. R. and Karo, W. (1974). *Polymer Syntheses. Volume 1*. Academic Press: New York and London. 3-17, 9-10.
- Schmidt, L., Sun, J. J. and Fritz, S. (1993). Solid-phase extraction of phenols using membranes loaded with modified polymeric resins. *J. Chromatogr.* 641: 57-61.

- Settle, F. A. (1997). *Handbook of Instrumental Techniques for Analytical Chemistry*. Prentice Hall PTR: Upper Saddle River, New Jersey. 35-40.
- Shalliker, R. A., Douglas, G. K., Comino, P. R. and Kavanagh, P. E. (1997). Examination of various pore size zirconias for potential chromatographic applications. *Powder Technology*. 91: 17-23.
- Sun, J. J. and Fritz, J. S. (1990). Chemically modified polymeric resins for high-performance liquid chromatography. *J. Chromatogr.* 522: 95-105.
- Sun, J. J. and Fritz, J. S. (1992). Chemically modified resins for solid-phase extraction. *J. Chromatogr.* 590: 197-202.
- Tuncel, A., Kahraman, R. and Piskin, E. (1993). Monosize polystyrene microbeads by dispersion polymerization. *J. Applied Polymer Science*. 50: 303-319.
- Vendula, R. R. and Spencer, H. G. (1991). Adsorption of polyacrylic acid on titania anatase and zirconia colloids. *Colloids Surf.* 58: 99-111.
- Vogelsang, U. B., Deege, A., Figge, H., Kohler, J. and Schomburg, G. (1984). Analytical Advantages of Highly Stable Stationary Phases for Reversed-Phase LC. *Chromatographia*. 19: 170.
- Weber, T. P. and Carr, P. W. (1990). Comparison of Isomer Separation on Carbon-Clad Microporous Zirconia and on Conventional Reversed-Phase High-Performance Liquid Chromatography Supports. *Anal Chem.* 62: 2620-2625.
- Wehrli, A., Hildenbrand, J. C., Keller, H. P., Frei, R. W. and Stampeli, R. (1978). Influence of organic bases on the stability and separation properties of reversed phase chemically bonded silica. *J. Chromatogr.* 149: 199.
- Yang, Y. B., Harrison, K. and Kindsvater, J., (1996). Characterization of a novel stationary phase derived from a hydrophilic polystyrene-based resin or protein. *J. Chromatogr. A*. 723: 1-10.

Yu, J. C., Jiang, Z. T., Liu, H. Y., Yu, J. and Zhang, L. (2003).  $\beta$ -Cyclodextrin epichlorohydrin copolymer as a solid-phase extraction adsorbent for aromatic compounds in water samples. *Analytica Chimica Acta*. 477: 93-101.

## LIST OF PUBLICATIONS

Parts of the work have been presented in the following scientific meetings and/or papers:

1. Norsyariza Abd Aziz, Ahmedy Abu Naim, M. Marsin Sanagi, Wan Aini Wan Ibrahim, Asiah Hussain, "Synthesis and Characterization of Nano Size Poly(Styrene-Divinyl Benzene) using Dispersion Copolymerization", Paper presented at *Symposium Kimia Analisis Malaysia Ke-18 (SKAM-18)* 12-14 September 2005, Hyatt Regency Hotel, Johor Bahru, Johor.
2. Mohd Marsin Sanagi\*, Sri Hilma Siregar, Ahmedy Abu Naim, Asiah Hussain and Shiv Prasad a/l Sandera Bahador, "Solid Phase Extraction of Organophosphorous Pesticides using Poly(styrene-divinylbenzene)-based Adsorbents" Paper presented at the *Annual Fundamental Science Seminar 2005 (AFSS 2005)*, 4-5 July 2005, Institut Ibnu Sina, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.
3. Mohd Marsin Sanagi, Mohd Sani Sarjadi, Ahmedy Abu Naim and Asiah Hussain, "Preparation and Characterization of Acetyl-modified Polystyrene-divinyl benzene) Adsorbents for Solid Phase Extraction", Paper presented at the *Annual Fundamental Science Seminar 2005 (AFSS 2005)*, 4-5 July 2005, Institut Ibnu Sina, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.
4. Mohd Marsin Sanagi\*, Mohd Sani Sarjadi, Ahmedy Abu Naim and Asiah Hussain, "Preparation and Characterization of 2-Zirconyl-2-Methylethane-Poly(Styrene-Divinyl Benzene) Chloride Adsorbents", Paper presented at the *Annual Fundamental Science Seminar 2005 (AFSS 2005)*, 4-5 July 2005, Institut Ibnu Sina, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.
5. Sri Hilma Siregar, Mohd Marsin Sanagi, Ahmedy Abu Naim, Asiah Hussain, and Tham Ee Mun, "Stearoyl Chloride-modification of poly(styrene-divinylbenzene) adsorbent for Solid Phase Extraction", Paper presented at the 17<sup>th</sup> Malaysian Symposium on Analytical Chemistry, 24-26 August 2004, Swiss-Garden Resort, Pantai Balok, Kuantan, Pahang.

6. Mohd Sani Sarjadi, Mohd Marsin Sanagi, Ahmedy Abu Naim and Asiah Hussain, "Preparation and characterization of acetyl-modified poly(styrene-divinylbenzene) as adsorbent for solid phase extraction", Paper presented at the 17<sup>th</sup> Malaysian Symposium on Analytical Chemistry, 24-26 August 2004, Swiss-Garden Resort, Pantai Balok, Kuantan, Pahang. (Submitted for publication in *Malaysian Journal of Analytical Sciences*)
7. Mohd Marsin Sanagi, Ahmedy Abu Naim, Asiah Hussain, Sri Hilma Siregar and Mohd Sani Sarjadi, "Development of Poly(Vinyl alcohol)-modified Poly(styrene-divinylbenzene) Adsorbents", Paper presented at the *Annual Fundamental Science Seminar*, Puteri Pan Pacific Hotel, Johor Bahru, 20-21 May 2003.
8. Mohd Marsin Sanagi, Ahmedy Abu Naim, Asiah Hussain, Sri Hilma Siregar and Mohd Sani Sarjadi, " Synthesis of Poly(styrene-divinylbenzene) Adsorbents: Effects of Type of Stirrer, Time of reaction, Surfactants and Stabilizers", Paper presented at the *Annual Fundamental Science Seminar*, Puteri Pan Pacific Hotel, Johor Bahru, 20-21 May 2003.